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# CHAPTER 5. POTENTIAL OF OILSEED RADISH AS A BIOENERGY CROP

## 5.1. Oilseed radish as a raw material for biofuel production

The development of bioenergy is also very relevant for Ukraine with its significant potential of local fuels available for energy production – biomass up to 24 million tons of equivalent fuel per year. Oilseeds from the cabbage family are important in this area. Most monographic publications, perspective programs for agricultural development in Ukraine and foreign countries assign oilseed radish a promising role in ensuring bioenergy security both in terms of biofuel production and processing of its leaf mass through biochemical fermentation to produce biogas (Table 5.1).

Table 5.1

**Potential productivity of oilseeds of the cabbage family – raw materials for phytodiesel (Tsytsiura, 2011)**

| Agricultural crops | Seed yield, t ha$^{-1}$ | Oil content, % |
|---|---|---|
| Rapeseed | | |
| winter | 1.5–4.5 | 45–50 |
| spring | 1.3–3.5 | 41–49 |
| Oilseed radish | 1.2–2.1 | 31–50 |
| Barbaréa vulgáris | | |
| winter | 1.5–2.5 | 43–47 |
| spring | 1.0–2.0 | 38–48 |
| Mustard | | |
| white | 1.0–2.2 | 35–47 |
| gray | 1.2–2.1 | 32–49 |
| Camelina spring | 0.6–2.9 | 33–41 |

One of the most promising areas in Ukraine's non-conventional energy sector is the use of phytodiesel and phytomass (Strategic directions, 2020). It is known that the seeds of high-oil crops (rapeseed, rape, mustard, flax and oil radish, safflower, chufa, camelina) are one of the most promising sources of alternative biodiesel based on the classification of oilseeds (Figure 5.1).

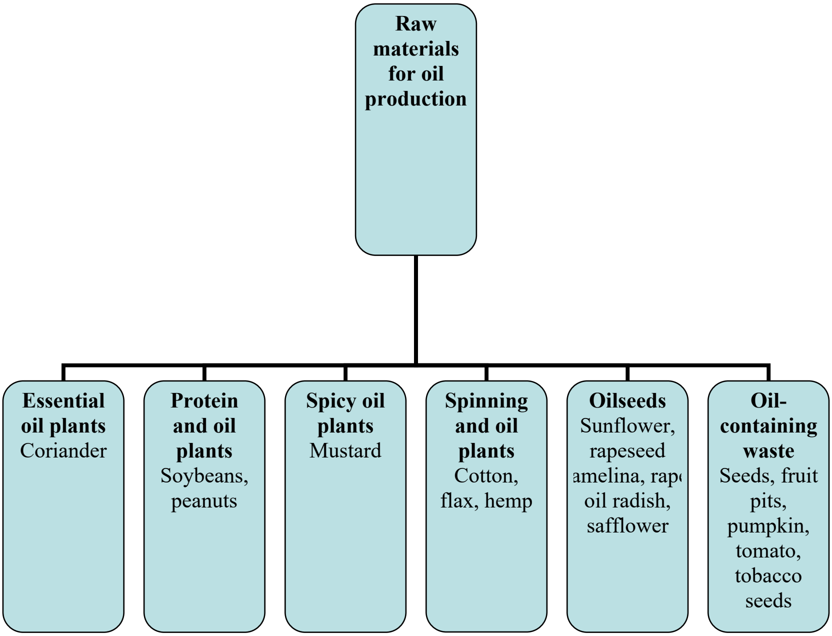



**Figure 5.1 – Classification of oilseeds (Polischuk, 2010)**

To date, Ukraine has created a collection of energy plants that includes about 350 taxa, and three areas of phytopower have been identified. The first area is feedstock crops based on highly productive, mostly perennial plants that provide phytomass for processing into solid biofuels or biomass or some other fuel, such as pyrolysis fuel. This group includes sorrel, perennial sida (up to 20 years old), whole-leaved silybum, elephant grass, perennial sorghum, etc. In total, this group includes 144 taxa. These include species, forms, and varieties of various crops.

The second large group includes crops that are selected in such a way that they are all high-oil crops. This includes 139 taxa. Among them are oil radish, winter and hybrid rape, camelina, etc. The third group includes plants used to produce phytoethanol – 71 taxa in total. These are sugar-containing plants, such as sugar sorghum, eucalyptus, chumizu, bubble sunflower or topin sunflower (a hybrid of sunflower and Jerusalem artichoke), etc.

If we make a comparative assessment of various oil-containing crops that can potentially be used for biofuel production (Figure 5.2), among 34 crops whose oil is to some extent a raw material for its production, oilseed radish ranks 18th with a productivity of 668 l $ha^{-1}$ of vegetable oil.

The first mention of oil radish as an oil plant in the official Soviet literature dates back to 1952 (Sharapov, 1952). Kovarsky (1952), who studied oil radish in the Kherson region and Moldova, noted that the costs of growing it were much lower than those of sunflower, and the oil yield was much higher. Its seed yield ranges from 10–15 to 20–30 c $ha^{-1}$, which, with a seed oil content of 40–50%, provides an oil yield of 0.5–1.0 t/ha.

The first thorough studies of oil radish oil were conducted in 1952–1955 by Cherep (1955). According to the results of her studies, oil radish oil resembles sunflower oil in appearance, has a mild taste and a light radish flavor. The author conducted an organoleptic evaluation of the oil of this crop, carried out qualitative reactions and elemental analysis, and determined its physical and chemical characteristics, which are presented in the Table. Based on the results of the presented data (iodine and radon numbers), the author classifies oil radish oil as a semi-drying oil. The low saponification number is explained by the presence of erucic acid in the composition. The determination of the fatty acid composition of the oil showed the following composition: saturated acids 12.16 %, unsaturated acids 87.84 %, of which linoleic acid 10.01 %, oleic and erucic acids (in total) 70.13 %.

For a more detailed characterization, the oil radish oil was subjected to thermal compaction (polymerization) (Table 5.2), which showed the relevant technical parameters of the oil's suitability for thermodynamic combustion processes in controlled pressure and temperature systems. These parameters were also confirmed during oxy-polymerization (heating of the oil with oxygen purge) of the oil with different degrees of heating (Table 5.3).

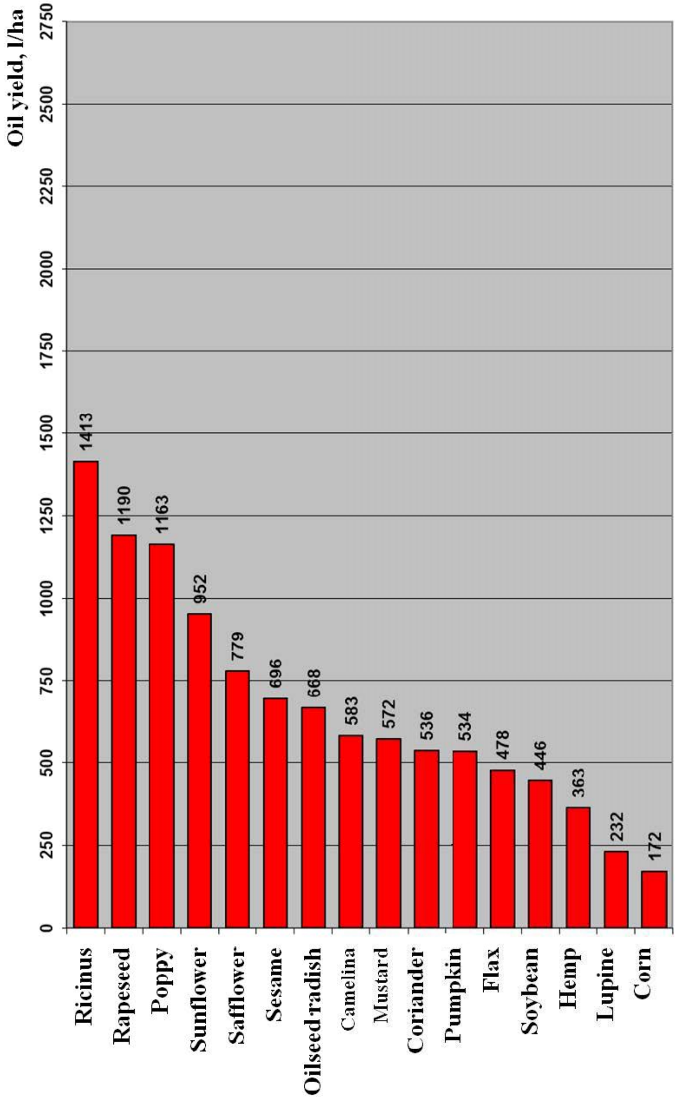



**Figure 5.2 – Oil yield for different crops, liters/ha (Tsytsiura and Tsytsiura, 2015)**

Table 5.2

## Main characteristics of oil radish oil (Cherep, 1955)

| Oil samples | Organoliptic properties | | | | |
|---|---|---|---|---|---|
| | Colour | Transparency | Color on the iodine scale | Smell | Taste |
| Cold pressed oil | Golden yellowish | After settling, all samples are absolutely transparent | 30 | Light radish shade | Soft, satisfactory with a radish flavor |
| Hot pressed oil | Golden yellowish with a darker shade | | 40 | | |
| Oil extracted with ether | Golden yellowish with a darker shade | | 35 | | |
| Oil extracted with ether and washed with water | Golden yellowish with a greenish tint | – | – | | |
| Oil extracted with gasoline | Golden yellowish with a darker shade | – | – | | |

After settling, all samples are absolutely transparent

| Oil samples | Specific gravity at $20^0$ C | Refractive index | Rotation of the polarization plane at 23 $^0$C | Viscosity in degrees of Engler | Specific viscosity in centipoise | Relative surface tension | Critical dissolution temperature in absolute alcoho$^0$C | The temperature of solidification, $^0$ C | Brencken flash point | Solubility in organic solvents |
|---|---|---|---|---|---|---|---|---|---|---|
| Cold pressed oil | 0.9153 | 1.4725 | -0.75$^0$ | 3.91 (59$^0$) | 69.33 | 0.4686 | 80 | 10 | 333$^0$ | Well soluble in all organic solvents in 96 % alcohol only when heatedi |
| Hot pressed oil | 0.9156 | 1.4725 | – | 3.99 (50$^0$) | 70.90 | 0.4578 | 78 | -17 | 320$^0$ | |
| Oil extracted with ether | 0.9159 | 1.4722 | – | – | 69.70 | 0.4509 | 79 | – | – | |
| Oil extracted with ether and washed with water | 0.91610 | 1.47220 | – | – | 74.33 | 0.4510 | 78 | – | – | |
| Oil extracted with gasoline | 0.9151 | 1.4722 | – | – | 73.52 | 0.4575 | 76 | – | – | |

(End of Table 5.2)

| Oil samples | Chemical parameters | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Acid number | Free acids in % per oleic acid | Saponification number | Airtime number | Iodine number | Rodan number | Amount of water-insoluble fatty acids (Genera number) | Amount of unsaponifiable substances | The amount of glycerin is calculated by the ether number |
| Cold pressed oil | 0.9 | 0.45 | 171.4 | 170.5 | 100.5 | 81.96 | 93.80 | 1.20 | 9.33 |
| Hot pressed oil | 1.1 | 0.55 | 170.0 | 168.9 | 103.2 | 82.99 | 92.47 | 1.32 | 9.24 |
| Oil extracted with ether | 2.3 | 1.15 | 170.0 | 167.7 | 101.8 | 82.62 | 93.99 | 1.22 | 9.17 |
| Oil extracted with ether and washed with water | 2.3 | 1.15 | 170.6 | 168.3 | 102.5 | 80.35 | 92.21 | 1.22 | 9.21 |
| Oil extracted with gasoline | 2.1 | 1.05 | 170.0 | 167.9 | 100.8 | 81.60 | 92.51 | 1.62 | 9.18 |

Table 5.3

**Physicochemical parameters of radish oil polymerized at a temperature of 280–300 0C (Cherep, 1955)**

| Oil samples | Heating time, h | The specific gravity $d^{20}_{20}$ | Refractive index at 23 °C | Acid number | Free acids per oleic acid, % | Saponification number | Airtime number | Iodine number |
|---|---|---|---|---|---|---|---|---|
| Control | – | 0.9150 | 1.4710 | 3.80 | 1.90 | 181.0 | 177.20 | 106.8 |
| Heated oil | 0.5 | 0.9182 | 1.4710 | 9.75 | 3.87 | 182.3 | 174.50 | 104.6 |
| | 2.5 | 0.9216 | 1.4715 | 14.30 | 7.15 | 184.0 | 169.70 | 98.0 |
| | 5.0 | 0.9261 | 1.4720 | 18.60 | 9.39 | 189.0 | 170.4 | 90.0 |
| | 7.5 | 0.9285 | 1.4730 | 21.74 | 10.87 | 191.4 | 169.66 | 84.6 |
| | 10.0 | 0.9299 | 1.4732 | 24.90 | 12.45 | 192.9 | 168.03 | 82.4 |
| | 12.0 | 0.9328 | 1.4733 | 26.30 | 13.15 | 189.3 | 163.0 | 71.7 |
| | 15.0 | 0.9342 | 1.4710 | 27.80 | 13.90 | 186.0 | 158.20 | 71.3 |
| | 17.5 | 0.9356 | 1.4750 | 30.81 | 15.40 | 184.8 | 153.99 | 65.3 |
| | 20.0 | 0.9374 | 1.4750 | 34.00 | 17.00 | – | – | 63.5 |
| Control | 0 | 0.9150 | 1.4730 | 3.49 | 1.75 | 178.5 | 175.01 | 106.8/0.13* |
| Oil blown with air at a temperature of 100–120 ⁰ C | 5 | 0.9156 | 1.4731 | 3.50 | 1.75 | 178.7 | 175.2 | 104.2/0.41 |
| | 10 | 0.9229 | 1.4735 | 3.62 | 1.81 | 180.0 | 176.38 | 98.4/0.56 |
| | 15 | 0.9238 | 1.4740 | 3.75 | 1.88 | 181.5 | 177.75 | 97.5/0.99 |
| | 20 | 0.9316 | 1.4748 | 3.82 | 1.91 | 181.6 | 177.78 | 90.0/0.48 |
| | 25 | 0.9368 | 1.4752 | 4.13 | 2.07 | 181.7 | 176.57 | 81.0/– |
| | 30 | 0.9443 | 1.4760 | – | – | – | – | 76.40/– |
| | 35 | 0.9500 | 1.4772 | 4.80 | 2.40 | 189.5 | 181.7 | 72.1/0.34 |
| | 40 | – | – | – | – | – | – | –/0.19 |
| | 50 | – | – | – | – | – | – | сліди |
| Control | 0 | 0.9150 | 1.4730 | 3.49 | 1.75 | 178.5 | 178.01 | 106.8/0.13* |
| Oil blown with air at a temperature of ратурі 130–150 ⁰ C | 5 | 0.9152 | 1.4732 | 3.41 | 1.76 | 178.9 | 175.49 | 104.3/0.13 |
| | 10 | 0.9200 | 1.4738 | 3.45 | 1.73 | 181.6 | 178.15 | 92.5/0.16 |
| | 15 | 0.9256 | 1.4748 | 3.52 | 1.71 | 182.1 | 178.58 | 91.2/0.25 |
| | 20 | 0.9324 | 1.4758 | 3.63 | 1.82 | 182.3 | 178.67 | 83.93/0.39 |
| | 25 | 0.9402 | 1.4768 | 4.19 | 2.10 | 183.7 | 179.51 | 74.8/0.24 |
| | 30 | 0.9444 | 1.4778 | 4.94 | 2.47 | 192.2 | 187.26 | 64.6/0.16 |
| | 35 | 0.9582 | 1.4782 | – | – | 193.3 | – | – |
| | 40 | 0.9642 | 1.4794 | 7.22 | 3.61 | 201.2 | 193.98 | 52.2/0.09 |

*– peroxide number.

According to the results of such a comprehensive study of oil radish oil, Cherep, as part of the production implementation already in the period 1954–1955, confirmed the possibility of using the oil of this crop, which can act as an effective substitute for alizarin oil, which can be successfully used for skin fatting in the form of an emulsion of oil radish oil or its sulfated product. These conclusions allow us to recommend oil radish oil as a substitute for castor and alizarin oil for the fatty acidification of natural leather.

Today, the biofuel use of this crop oil is extremely promising. Ukraine, unfortunately, is only at the stage of actively starting to study this crop as a component of the biofuel market. Among the CIS countries, the Russian Federation, in particular the southern and central regions of the country, is a leader in this area. In European countries, the direction of using oil from oil radish for the production of alternative fuels is actively developed by Germany, Poland, and the UK, where varieties with high oil content in seeds are being created.

It should also be noted that oil radish forms a large phytomass, which in turn can be used as green manure and for fermentation to produce biogas. Between 2000 and 2024, its area in Europe and the United States (northern states) almost tripled compared to 1990. In particular, Landkom is actively engaged in growing oil radish in Europe and South Africa. In the United States, the center for the study of vegetable oil from radish is the state of Georgia (UGA College of Agricultural and Environmental Sciences).

The research of scientists at this institution notes that oil radish is an extremely promising non-food crop for the production of alternative fuels. The seeds of this crop contain 40-45% of vegetable oil, which is similar in chemical composition to rapeseed oil and has a wide range of economic uses, making it an excellent candidate for the biodiesel market.

These conclusions are confirmed by Shpaar (2006) and others (Moiseeva, 2006), noting that the technical direction of using its oil is determined by the content of simple unsaturated fatty acids (in % of the total fatty acid content – aicosene (8–11 %) oleic (23–36 %), erucic (9–30 %)), high content of saturated oleic acid (4–6 %), low content of multiple unsaturated linoleic (10–18 %) and linolenic (11–17 %) fatty acids (Tables 5.4–5.7, Figure 5.3).

It should be noted that in Ukraine, at present, the industrial processing of oil radish according to the “pressing – extraction” scheme for the production of technical oil is complicated by the lack of regulatory and technical documentation (DSTU, TU, etc.) for oil and meal made from it (Tsytsiura, 2011).

Table 5.4

**Characteristics of oilseeds and fatty acid composition of oils (Polishchuk, 2010)**

| Crops | Botanical family | Variety type | Content, % | | Fatty acid sweetness of oils, % to total fatty acid content | | | | | | | Glucosinolates content, µmol g$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Fat | Protein | $C_{16:0}$ palmettine | $C_{18:0}$ stearic | $C_{18:1}$ oleic | $C_{20:1}$ aicosene | $C_{22:1}$ eruca | $C_{18:2}$ linoleum | $C_{18:3}$ linolenic | |
| Rape | Cruciferous | ++ | 37 – 47 | 22 – 25 | 2 | 1 | 1 | 7 | 50 | 15 | 7 | 55 – 75 |
| | | 00 | 39 – 48 | 22 – 25 | 3 – 5 | 1 – 2 | 58 – 62 | 0 – 1 | 0 – 1 | 18 – 22 | 9 – 11 | 6 – 13 |
| Sarepta mustard | Cruciferous | ++ | 22 – 39 | 29 – 35 | 2 – 4 | 1 – 2 | 8 – 20 | 7 – 12 | 21 – 40 | 15 – 23 | 13 – 16 | 19 |
| | | 00 | 22 – 39 | 29 – 35 | 4 | 2 | 39 | 1 | 0 | 40 | 13 | 19 |
| Sunflower | Asteraceae | Normal type | 36 – 55 | 14 – 22 | 5 – 6 | 4 – 7 | 14 – 20 | – | – | 67 – 73 | – | – |
| Oil flax | Flax | – | 42 – 52 | 16 – 23 | 4 – 6 | 2 – 5 | 15 – 25 | – | – | 11 – 19 | 50 – 68 | – |
| Hemp | Mulberry | – | 33 – 55 | 22 – 26 | 6 | 3 | 11 | – | – | 58 | 21 | – |
| Safflower | Asteraceae | Normal type | 18 – 50 | 12 – 18 | 2 – 6 | 1 – 4 | 14 – 24 | – | – | 63 – 79 | – | – |
| Oilseed radish | Cruciferous | + | 35 – 39 | 25 – 30 | 4 – 6 | 2 – 3 | 23 – 36 | 8 – 11 | 9 – 30 | 10 – 18 | 11 – 17 | 160 – 180 |
| Oil poppy | Poppy | – | 40 – 55 | 20 – 28 | 10 – 12 | 0 – 1 | 12 – 22 | – | – | 60 – 75 | 0 – 1 | – |
| Pumpkin | Pumpkin | – | 40 – 58 | 34 – 38 | 7 – 12 | 6 – 8 | 20 – 40 | – | – | 45 – 60 | – | – |
| Lalemantia | Lip-flowering | – | 28 – 38 | 26 – 29 | 4 – 6 | 1 – 3 | 9 – 11 | 1 – 2 | – | 60 – 70 | 1 – 4 | – |
| White mustard | Cruciferous | ++ | 24 – 34 | 27 – 33 | 2 – 4 | 1 – 2 | 15 – 36 | 6 – 12 | 24 – 57 | 7 – 13 | 9 – 11 | 240 – 290 |
| | | 00 | 30 – 36 | 27 – 33 | 2 – 3 | 1 – 2 | 58 – 62 | 2 – 3 | 0 – 1 | 12 – 16 | 17 – 18 | 4 – 7 |
| | | +0 | 36 – 38 | 27 – 33 | 2 – 3 | 1 – 2 | 10 – 12 | 2 – 4 | 55 – 59 | 9 – 10 | 14 – 15 | 10 – 15 |

Variety types: ++ – with erucic acid and glucosinolates (old forms); 00 – without erucic acid and glucosinolates

Table 5.5

**Chemical composition of oil of some oilseeds according to D. Shpaar (2006)**

| Crops | Sort type | Content oils, % | Composition of important fatty acids in oils, % of total fatty acid content: saturated fatty acids | | simple unsaturated fatty acids | | | multiply unsaturated fatty acids | | Protein content, % | Gluco-einolatse content, µmol $g^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Rapeseed | ++ | – | 3–4 | 1–2 | 12–23 | 9–14 | 41–47 | 15–25 | 10–15 | – | 55–75 |
| | ++ | 37–47 | 2 | 1 | 1 | 7 | 50 | 15 | 7 | – | – |
| | 00 | 39–48 | 3–5 | 1–2 | 58–62 | 0–1 | 0–1 | 18–22 | 9–11 | 22–25 | 6–13 |
| Sarepitsa | ++ | – | 2–3 | 1–2 | 17–34 | 10–12 | 24–40 | 14–18 | 9–11 | – | 70 |
| | ++ | 36–46 | 1–3 | 1–2 | 10–27 | 8–12 | 27–52 | 13–22 | 7–11 | – | – |
| | 0+ | 37–47 | 3–5 | 1–2 | 54–60 | 0–2 | 0–2 | 18–23 | 11–14 | 22–26 | 45–55 |
| | 00 | – | 3–4 | 1–2 | 55–57 | 1–2 | 0–2 | 21–23 | 13–14 | – | < 10 |
| Sarepta mustard | ++ | 30–40 | 1–4 | 1–4 | 28–34 | 1–3 | 20–45 | 15–20 | 2–5 | – | – |
| | ++ | 23–39 | 3 | 1 | 2 | 7 | 47 | 16 | 11 | 29–35 | – |
| | ++ | – | 2–4 | 1–2 | 8–20 | 7–12 | 21–40 | 15–23 | 13–16 | – | – |
| | 00 | 44 | 4 | 2 | 39 | 1 | 0 | 40 | 13 | – | 19 |
| Black mustard | ++ | 24–38 | 2–4 | 1–2 | 8–19 | 7–12 | 24–43 | 13–23 | 13–16 | – | 55–120 |
| White mustard | ++ | 24–34 | 2–4 | 1–2 | 15–36 | 6–12 | 24–57 | 7–13 | 9–11 | 27–33 | 240–290 |
| | 00 | ок.30 | 2–3 | 1–2 | 58–62 | 2–3 | 0–1 | 12–16 | 17–18 | – | 4–7 |
| | +0 | 36–38 | 2–3 | 1–2 | 10–12 | 2–4 | 55–59 | 9–10 | 14–15 | – | 10–15 |
| Radish oilseed | ++ | 35–39 | 4–6 | 2–3 | 23–36 | 8–11 | 9–30 | 10–18 | 11–17 | – | 160–180 |
| Crumbe | ++ | 31–41 | 1–2 | 0,5–1 | 14–18 | 2–5 | 54–62 | 7–9 | 4–7 | 16–23 | 60–120 |

Our studies have also shown that oil radish seeds have a high fat content (on a dry matter basis) ranging from 34 to 38%, depending on the variant, and a relatively high protein content of 22.4 to 23.8%. 1 kg of dry matter of seeds contains more than 1 k.e. with a content of 170.3–185.3 g of digestible protein in each (Table ). At the same time, it was noted (Maksymuk et al., 2009) that burning 1 g of rape seeds yields 26.9 J of energy, oil flax – 26.2; spring rape and camelina – 25.5; oil radish – 25.1; gray mustard – 24.3; white mustard – 22.8 J of energy.

Table 5.6

**Fatty acid composition of vegetable oils, % (Kozlenko, 2011)**

| Acid | Short chemical formula | Spring rapeseed | Rocket-cress | White mustard | Sarepta mustard | Oilseed radish | Camelina spring | Safflower | Oil flax |
|---|---|---|---|---|---|---|---|---|---|
| Kaprinova | 10: 0 | Traces* | Traces | Traces | Traces | – | – | – | – |
| Laurinova | 12:0 | Traces | Traces | 0.01 | 0.01 | Traces | – | – | – |
| Miristinova | 14:0 | 0.08 | 0.08 | 0.03 | 0.07 | 0.10 | 0.08 | 0.14 | 0.06 |
| Palmitic | 16:0 | 3.46 | 2.55 | 2.21 | 2.28 | 4.96 | 4.60 | 4.75 | 3.93 |
| Palmito-oleic | 16:1 | 0.18 | 0.22 | 0.17 | 0.28 | 0.18 | 0.14 | 0.12 | 0.10 |
| Stearic | 18:0 | 1.95 | 1.66 | 0.93 | 1.20 | 2.38 | 2.22 | 1.86 | 4.27 |
| Oleic | 18:1 | 65.70 | 51.21 | 31.84 | 33.22 | 37.43 | 14.99 | 8.74 | 15.36 |
| Linoleic | 18:2 | 19.14 | 20.42 | 8.60 | 8.37 | 15.97 | 17.18 | 82.46 | 12.30 |
| Linolenic | 18:3 | 8.44 | 15.77 | 22.08 | 22.53 | 23.92 | 54.00 | 0.85 | 63.30 |
| Eicosenic | 20:1 | 0.26 | 0.31 | 0.43 | 0.54 | 0.65 | 1.73 | 0.17 | 0.10 |
| Begenic | 22:0 | 0.33 | 0.28 | – | 0.32 | 0.29 | 1.78 | 0.27 | 0.29 |
| Erukova | 22:1 | 0.16 | 6.98 | 31.51 | 29.23 | 12.64 | 3.00 | 0.08 | 0.29 |
| Karnaubovic | 24:0 | – | 0.25 | 0.37 | 0.16 | 0.12 | 0.06 | 0.03 | – |
| Nervonic | 24:1 | 0.30 | 0.27 | 1.82 | 1.79 | 1.36 | 0.22 | 0.53 | – |
| Total | | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

* Traces – the content of this acid will be approximately less than 0.01 %.

In addition, we have determined that oil radish seeds are a potentially possible high-energy feed, 1 kg of dry matter of which provides 15.9 – 16.6 MJ of metabolizable and 26.1–27.3 MJ of gross energy.

Studies of the physicochemical properties of oil radish oil have shown that it is a semi-dry oil. During processing, the oil is well hydrated and can be successfully used in the production of margarine and soap. According to Cherepa (1952), the hydrogenation of oil radish oil resulted in salomas with a melting point of 55 °C and a titer (fatty acid pour point) of 53 °C. The saponification coefficient of the salomas is 183. The filtered product can be successfully used for soap making. Straw with a melting point of 32–36 °C can be used in unlimited quantities for margarine production. Moreover, straw from oil radish seeds was not inferior to a similar product obtained from other vegetable oils processed into margarine and soap.

Table 5.7

**Experimental value of specific heat of combustion for raw materials of some oilseeds (De Andrade et al., 2012)**

| Crops | Maximum value of calorific value, MJ kg$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | oil (O) | Fatty acid methyl esters (FAME) | FAME-O | Fatty acid ethyl esters (FAEE) | FAEE-FAME |
| Oilsed radish | 39.72 | 40.04 | 0.32 | – | – |
| Mustard | 40.07 | 40.25 | 0.18 | – | – |
| Rocket-cress | 40.09 | 40.28 | 0.19 | – | – |
| Rapeseed | 39.6 | 39.87 | 0.27 | 40.12 | 0.25 |
| Sunflower | 39.46 | 39.71 | 0.25 | 39.80 | 0.09 |
| Oil flax | 39.51 | 40.00 | 0.49 | 39.65 | -0.35 |

The results of the chromatographic determination of the fatty acid composition of oil radish seeds of ‘Zhuravka’ and ‘Raduga’ varieties are presented in Table 5.8.

Our results confirm the category of oil for both varieties as semi-drying for technical purposes. A high variability of fatty acid composition of oil radish seeds was noted over the years of study. Thus, for the Zhuravka variety, the content of palmitoleic acid was not detected on the chromatogram at all in 2010 and 2012.

The situation is similar with caprylic, eicosatrin and ellaidic acids. Similar features were noted for some acids for the ‘Raduga’ variety. Based on this, it was noted that the fatty acid composition of cruciferous seeds depends on weather conditions, doses of mineral fertilizers, varietal characteristics of soil nutrition, and the nature of the accumulation of acids can change towards a higher content of certain acids within close values of their molecular index. Therefore, this issue for oil radish requires additional detailed further study.

By comparing the chemical characteristics of vegetable oils for technical use with the results established for oil radish, we proved the possibility of its use for biofuel production (Tsytsiura, 2013). We have also found that oil radish at the first sowing date with a sowing rate of 2 million seeds per hectare of germinating seeds provides oil yields in the range of 0.17–0.28 t $ha^{-1}$, depending on the variety and level of seed yield on an unfertilized background and 0.59–0.80 t $ha^{-1}$ on a background with $N_{60}P_{60}K_{60}$. At a sowing rate of 1.5 million units/ha of germinating seeds, these figures were 0.28–0.69 and 0.61–1.02 t $ha^{-1}$, respectively.

Table 5.8

**Chemical composition and nutritional value of seeds of oilseed radish varieties under different fertilization (Tsytsiura and Tsytsiura, 2013)**

| Seeding rate, mln. units $ha^{-1}$ of germinating seeds | Fertilizers | Content in completely dry substance, % | | | | | Dry matter, % | Content per 1 kg of dry matter | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | protein | fat | fiber. | ashes | Nitrogen-free extractives | | Feed units* | Digestible protein, g | Metabolic energy, MJ | Gross energy, MJ |
| ‘Zhuravka’ (average for 2010–2012) | | | | | | | | | | | |
| 2,0 | Without fertilizers | 23.6 | 36.9 | 17.3 | 6.2 | 15.3 | 93.0 | 1.02 | 181.0 | 15.8 | 26.5 |
| | $N_{60}P_{60}K_{60}$ | 23.9 | 37.8 | 17.1 | 6.5 | 15.6 | 92.7 | 1.01 | 183.7 | 16.1 | 26.9 |
| ‘Raduga’ (average for 2010–2012) | | | | | | | | | | | |
| 2,0 | Without fertilizers | 22.4 | 37.5 | 17.0 | 5.1 | 16.5 | 93.3 | 1.03 | 170.3 | 15.9 | 26.6 |
| | $N_{60}P_{60}K_{60}$ | 23.6 | 37.9 | 18.6 | 5.2 | 16.3 | 94.1 | 1.02 | 180.6 | 16.0 | 27.3 |

* – the content of feed units was adjusted for the potential nature of the food.

At the same time, the yield of biofuel from oil at the actual seed yield, according to technical standards, was 0.37–0.42 t/ha against the background of N60P60K60 application (Table 5.8).

The bioenergy evaluation of oil from oilseed radish is also highly efficient (Table 5.9).

To obtain oil from oil radish seeds, both cold and hot pressing technologies are used. The technology of cold pressing, cold pressing of vegetable oil, produces raw materials for further production of biodiesel fuel.

The oil is also used in the pharmaceutical industry. Cold pressing takes place at a temperature of at least 50 degrees Celsius. With hot pressing technology, the mass of seeds is crushed, heated and pressed at the same time. The pressed mass is divided into vegetable oil and cake. The oil content of the raw material should be at least 15%, of warehouse condition (weed-free, medium dry) (Andreeva, 2007; Oseiko, 2006; Shevchuk et al., 2011).

Table 5.9

**Fatty acid composition of seeds of oil radish varieties of the first sowing term on unfertilized background, 2010–2012 (Tsytsiura, 2010)**

| Formula IUPAC | Fatty acids | 'Zhuravka' | | | 'Raduga' | |
|---|---|---|---|---|---|---|
| | | 2010 | 2011 | 2012 | 2011 | 2012 |
| $C_{8:0}$ | Kaprilova | – | – | 0.48 | – | – |
| $C_{11:0}$ | Undekanova | 0.20 | 0.54 | 0.84 | – | 0.19 |
| $C_{16:0}$ | Palmitic | 5.62 | 6.04 | 6.09 | – | 5.46 |
| $C_{16:1}$ | Palmitoleic | – | 0.15 | – | 0.13 | 0.14 |
| $C_{18:0}$ | Elaidinic | 30.56 | – | – | – | – |
| $C_{18:0}$ | Stearic | 2.03 | 2.19 | 2.38 | 3.41 | 2.38 |
| $C_{18:1}$ | Oleic | 1.72 | 30.72 | 31.27 | 32.21 | 33.21 |
| $C_{18:2}$ | Linoleic | 16.34 | 17.79 | 17.18 | 17.82 | 16.98 |
| $C_{18:2}$ | Linoleoylaidiene | – | 1.70 | 2.30 | 2.40 | – |
| $C_{18:3}$ | Linolenic | 9.63 | 9.26 | 13.17 | 13.57 | 10.28 |
| $C_{20:0}$ | Arachinic | 0.79 | 0.09 | 0.79 | 0.85 | 0.11 |
| $C_{20:1}$ | Aikosenic | 13.60 | 14.23 | 0.16 | – | 13.98 |
| $C_{20:2}$ | Eicosadienoic | 0.86 | 0.96 | 10.79 | 11.70 | 0.64 |
| $C_{20:3}$ | Eicosatrinic | – | 14.10 | – | – | 0.11 |
| $C_{22:0}$ | Begeneva | 0.35 | 0.33 | 0.32 | 0.39 | 0.43 |
| $C_{22:1}$ | Erukova | 16.28 | 0.13 | 12.87 | 15.40 | 14.22 |
| $C_{22:2}$ | Docosadiene | 0.48 | 0.40 | – | – | 0.51 |
| $C_{24:0}$ | Lignoceric | 1.52 | 1.21 | 0.42 | 0.54 | 1.37 |
| $C_{24:1}$ | Nervonova | – | 0.16 | 1.42 | 1.58 | – |

Notes: 1. Saturated fatty acids are in italics; 2. IUPAC – International Union of Pure and Applied Chemistry.

The method of producing oil from oil radish (cold or hot pressing, extraction) is crucial in changing its biological value. During hot pressing, the raw material is heated to 105–120 ºC. During extraction, hexane or gasoline is used as a solvent, which is subsequently eliminated, but some of it still remains in the final product, absorbents and alkali are used. This production method makes the oil lighter and more transparent, and allows the use of raw materials of different quality. Experts say that heating deforms the linoleic acid molecule. Such a molecule can still serve as a fuel, but it loses its vitamin role and is unable to penetrate the delicate structures of human tissues. The difference between the two molecular structures, before and after heating the oil, is similar to that between starch and cellulose. The former can be eaten, while the latter cannot. Oil produced by hot pressing or extraction turns into a "dead" product devoid of biological value.

Table 5.10

**Oil yield of oil radish varieties depending on seeding rate and fertilization at the first sowing term, t ha$^{-1}$ (Tsytsiura, 2011)**

| Fertilizers | 'Zhuravka' (2010–2012) | | | | 'Raduga' (2011–2012) | | | |
|---|---|---|---|---|---|---|---|---|
| | output, t ha$^{-1}$ | | | | | | | |
| | for biological seed yield | | with the actual seed harvest | | for biological seed yield | | with the actual seed harvest | |
| | oil | biofuels from oil | oil | biofuels from oil | oil | biofuels from oil | oil | biofuels from oil |
| | 2 million units ha$^{-1}$ of germinating seeds | | | | | | | |
| Without fertilizers | 0.28 | 0.17 | 0.17 | 0.12 | 0.27 | 0.16 | 0.20 | 0.12 |
| $N_{60}P_{60}K_{60}$ | 0.80 | 0.50 | 0.59 | 0.40 | 0.73 | 0.44 | 0.57 | 0.37 |
| | 1.5 million units ha$^{-1}$ of germinating seeds | | | | | | | |
| Without fertilizers | 0.69 | 0.41 | 0.39 | 0.23 | 0.42 | 0.25 | 0.28 | 0.17 |
| $N_{60}P_{60}K_{60}$ | 1.02 | 0.61 | 0.67 | 0.42 | 0.86 | 0.52 | 0.61 | 0.39 |
| *$LSD_{05total}$, t ha$^{-1}$* | | | 0.31 | | | | 0.26 | |

Table 5.11

**Oil yield and bioenergy estimation from seeds of spring oilseeds at average levels of seed productivity (Kozlenko, 2011)**

| Crops | Oil content in seeds, % | Oil yield, t ha$^{-1}$ | Caloric content of oil, MJ kg$^{-1}$ | Energy yield with oil | |
|---|---|---|---|---|---|
| | | | | GJ ha$^{-1}$ | the equivalent amount of diesel fuel, l |
| Spring rape | 43.69 | 1.19 | 39.55 | 47.06 | 1312 |
| Barbaréa vulgáris | 29.42 | 0.47 | 39.29 | 18.47 | 515 |
| White mustard | 25.55 | 0.66 | 40.56 | 26.77 | 746 |
| Sarepta mustard | 38.00 | 0.84 | 38.74 | 32.54 | 907 |
| Oilseed radish | 29.18 | 0.59 | 41.42 | 24.44 | 681 |
| Camelina | 49.73 | 1.14 | 38.22 | 43.57 | 1215 |
| Safflower | 26.55 | 0.50 | 39.7 | 19.85 | 553 |
| Oil flax | 43.57 | 1.02 | 37.52 | 38.27 | 1067 |

* – The calculations were made taking into account the caloric content of diesel fuel at 35.87 MJ l$^{-1}$.

Cold pressed oil does not require refining and deodorization (temperature 230-240°C), which destroy natural vitamins and deform essential fatty acid molecules, since during cold pressing (temperature no more than 50°C), harmful waxes and paraffins do not melt as they do during hot pressing (temperature 105-120°C) and do not pass into the oil, but remain in the cake.

In terms of ensuring efficient oil radish seed hulling and oil extraction, it is advisable to use special designs of hullers (Shevchuk et al., 2011) adapted to the physical parameters of oil radish seeds.

## 5.2. Evaluation of biofuels derived from oilseed radish

Fossil fuel reserves are non-renewable and finite. Several researchers report clear indications of depleting fossil fuel resources. According to estimates, the global recoverable oil reserves are diminishing at a rate of 4 billion tonnes per annum. Even if it is assumed that the depletion of these reserves continue at the present rate, it is projected that all of these reserves will be exhausted by 2060 (Saini, 2021; Saleem, 2022).

According to the forecasts of the International Energy Association (IEA), the world production of biofuels will increase by 2030 to 92–147 million tons of energy equivalent of oil. The annual growth rate of biofuel production will be 7–9%. It is expected that by 2030 the consumption of biofuels in the countries of the European Union (EU) will increase by 13–18 times compared to current indicators (Brown et al., 2020; Global biofuels…, 2022). Europe is currently the biggest consumer of bio-based diesel (i.e., biodiesel called Fatty Acid Methyl Ester or FAME and renewable diesel or HVO) in the world. This is driven by the EU's targets for renewable energy in transportation coupled with a dominant share of diesel in this sector. Both factors will continue through 2030, resulting in increased demand for bio-based diesel, from 17.9 million tonnes (20.6 billion liters) in 2020 to 22.9 million tonnes (27.1 billion liters) in 2030. In Latin America where, along Asia, the growth in consumption of diesel by 2030 is projected to be the highest in the world, demand for biodiesel will grow as well from 7.4 million tonnes (8.4 billion liters) currently to 12.7 million tonnes (14.5 billion liters) by 2030 (Global biofuels…, 2022). Urthermore, to reduce dependency on petroleum, several international agencies and governments aim to use biofuels to supply 25% of their transportation energy by 2050 (Global biofuels…, 2022; Ilić & Ödlund, 2022; Malins & Sandford, 2022). A number of biofuel national programmes have been implemented to reduce importation of fossil fuels to enhance the security of national fuel supplies. (Valdivia et al., 2016; Ramos et al., 2022).

A number of crops are grown specifically for biofuel production and are known as energy crops. Its vary according to geography: for example, corn, soybeans, willows and switchgrass are common energy crops in the United States; rapeseed, wheat, sugar beet and willows are preferentially grown in northern Europe; sugarcane is grown in Brazil; palm oil and Miscanthus giganteus are grown in Southeast Asia; and sorghum and cassava are grown in China (Anand et al., 2019; Kaletnik et.al., 2021; de Lacerda et al., 2020).

Raw materials are needed to increase the production of biofuels. The problem of shortage of raw materials will intensify as processing capacities in Europe increase. The average utilization of biodiesel production capacities introduced in the EU in recent years reaches only 75–80% (Saleem, 2022). In addition, climate change, which means a decrease in the adaptability of several wide-spread bioenergy crops, suggests a search for alternative crops with a high biofuel potential (Karmakar & Halder, 2019; Ramos et al., 2022). In the rest of the years, the replication of such crops has significantly expanded the resistance of new species and the assessment of their potential is insufficiently explored (Puricelli, 2020; Pasha et al., 2021; Torroba, 2021; Neupane et al., 2022). This especially applies to the issues of finding out the technical parameters of oil suitability for application in classic diesel engine schemes (Faria et al., 2018; Ilić & Ödlund, 2022). It was for these reasons that the aim of our research was to study oilseed radish as an agricultural crop with a high potential for oil production, which is considered as a possible component of mixed biofuels.

We will present the results of the author's research from the perspective of assessing the potential of oil radish oil as a raw material base for biofuel production (Tsytsiura, 2023). Seed of high productive 12 oilseed radish (*Raphanus sativus* L. var. *oleiformis* Pers.) varieties was used for investigation such as 'Alpha', 'Olga', 'Ramonta', 'Iveya', 'Fakel', 'Raiduha', 'Zhuravka', 'Snizhana', 'Nika', 'Tambovchanka', 'Lybid', 'Sabina'. The varieties were of different selection and of different ecological and geographical origin (temperate-continental, continental, moderately arid zones). The zonal technology of oilseed radish cultivation was applied: sowing date was April 8-12, sowing rate of 1.5 million germinable seeds $ha^{-1}$, row width 30 cm, fertilizer rate $N_{60}P_{60}K_{60}$ (pre-sowing application).

The content of moisture, ash, lipid, protein and fiber in the oilseed radish seeds were determined by the AOCS (2017) and expressed on absolutely dry weight basis.

Solvent extraction (SE) (for chromatographic analysis) (according to Zhao et al., 2017) oilseed radish seed powder was prepared by grinding portions of the seeds in a grain mill (BiOloMix N-700Y) for 25 s. The seed powder (1000 g) was subsequently soaked in 5000 mL of n-hexane for 5 h at 25 °C and filtered. The residue obtained was again extracted with 5000 mL of n-hexane. The supernatants from both steps were collected, combined and concentrated by using Rotary evaporator under vacuum at 40 °C to remove nhexane. The oil obtained was weighed and stored at 4 °C prior to analysis.

The research was conducted using the most widespread in the region, the oilseed radish variety 'Zhuravka'. Research was conducted during 2015-2020 in the certified and accredited laboratory of the quality of raw oil and fat of Vinnitsa oil seeds crushing factory (private joint stock company). All determinations were made in quadruplicate. Oil from the seeds of this variety was used for the analyses obtained by the cold pressing method. A Klarstein Olivia cold press with an internal filtration system was used. Additionally, the oil was settled for 24 hours before analysis and passed through afilter of non-woven carbon fiber material (Karbopon brand).

According to the tested and standard methods, the following oil indicators were determined: density at 20 °C (ASTM D7042-04), refractive index (ASTM D1218), oil colour and rotation of the plane of polarization at 23 °C (Paquot & Hauntfenne (1992)), specific viscosity at 20 °C (ASTM D445), kinematic viscosity of oil at 20 °C (ASTM D445), relative surface tension (ASTM D971-12), carbon residue (wt.%) (ASTM D4530), net calorific value (ASTM D240), solidification temperature (ASTM D97), flash point (ASTM D93), solubility in organic solventsdensity (ASTM F739)), acid value (ASTM D 974), content of free acids in % of oleic acid (according to the results of chromatography of the fatty acid composition), saponification value (ASTM D664), ether value (Firestone (2013)), iodine value (ASTM D5768), rhodan value (Paquot & Hauntfenne (1992)), amount of water-insoluble fatty acids (gener number Firestone (2013)), amount of unsaponifiable matter (Paquot & Hauntfenne (1992)), sulfur content (ASTM D5453)).

To evaluate the change in the physicochemical properties of the oil, it was polymerized by thermal heating at 280 °C (an Industrial 500ML High Pressure Blender Stirred Autoclave Vessel Chemical Hydrothermal Synthesis Reactor was used). Changes in the physico-chemical properties of oil during its oxypolymerization (heating of oil with oxygen purging) were also studied using the same device as during polymerization with oxygen supplied under a pressure of 1 atm when heated at two modes of 120 °C and 150 °C within half an hour. Oil without oxypolymerization was heated to a temperature of 120 °C with a duration of holding at this level of temperature for half an hour. Polymerization and oxypolymerization of oil was carried out taking into account methodical approaches in accordance with Rinaldi et al. (2017). Polymerized and oxypolymerized oil was studied according to the main physicochemical parameters during its long-term heating for 1, 2, and 3 hours on the same laboratory equipment. As a control, a polymerized oil sample without additional heating was used.

Determination of the fatty acid composition of the seed oils of mentioned above varieties was conducted out by the method of gas-liquid chromatography using chromatograph Shimadzu GC 2014 (Japan) (according to Clancy, 2013; Hübschmann, 2018) with methyl heptadecanoate standard at a concentration of 9.8 mg $mL^{-1}$ for analysis of fatty acid composition. Samples were prepared using approximately 15 mg of product (oil), 200 µL of standard solution containing 9.8 µg of methyl heptadecanoate per 1000 µL and 1 mL of heptane (solvent). The configuration was set: SPL-2014 injector, FID-2014 flame ionization detector + TCD-2014 thermal conductivity detector. Identification of fatty acids was carried out by comparing the received chromatograms with chromatograms of such standard solutions as methyl esters of fatty acids $C_6$-$C_{24}$.

Coefficients of ER (elongation ratio, Formula 5.1), DR (desaturation ratio, Formula 5.2), ODR (oleic desaturation ratio, Formula 5.3), LDR (linoleic desaturation ratio, Formula 5.4), saturated and unsaturated fatty acid ratio (Formula 5.5) were estimated (according to Velasco et al. (1998), Pleines & Friedt, 1988). Fatty acid ratios were estimated according to Blume et al. (2018).

$$ER = \frac{(\%)C20:1 + (\%)C22:1}{(\%)C20:1 + (\%)C22:1 + (\%)C18:1 + (\%)C18:2 + (\%)C18:3} \quad (5.1)$$

where here and formulas (2-4) (%)C20:1, C22:1 – content of the corresponding fatty acid in %.

$$DR = \frac{(\%)C18:2 + (\%)C18:3}{(\%)C20:1 + (\%)C22:1 + (\%)C18:1 + (\%)C18:2 + (\%)C18:3} \quad (5.2)$$

$$ODR = \frac{(\%)C18:2 + (\%)C18:3}{(\%)C18:1 + (\%)C18:2 + (\%)C18:3}, \quad (5.3)$$

$$LDR = \frac{(\%)C18:3}{(\%)C18:2 + (\%)C18:3} \quad (5.4)$$

$$S/U = \frac{Saturated\ \ fatty\ \ acids}{Unsaturate\ d\ fatty\ \ acids}; \quad (5.5)$$

$$PU/MU = \frac{Polyunsatu\ \ rated\ \ fatty\ \ acids}{Monounsatu\ \ rated\ \ fatty\ \ acids}. \quad (5.6)$$

International terminology (CODEX, 2020) was used for the components of oilseed radish vegetable oil found during the analysis.

Research was carried out during 2015–2020 on the research field (arranged by coordinates N 49°11′31″, E 28°22′16″) located in the zone of the Right-bank Forest-Steppe of Ukraine. The soil cover of the research field was represented by gray forest soils with the following agrochemical parameters (for the period of crop rotation): humus 2.02–3.20%, mobile forms of nitrogen 67–92 mg $kg^{-1}$, phosphorus 149–220 mg $kg^{-1}$, potassium 92–126 mg $kg^{-1}$ with metabolic acidity of soil solution (pHкcl) 5.5–6.0. The temperature regime and the humidification regime for the period of research for the growth of oilseed radish plants had significant differences. This allowed to analyze the influence of weather conditions on the fatty acid composition of oil in oilseed radish varieties. According to the weather conditions stress effect on the processes of seed formation of oilseed radish plants for years of observation 2015-2020 can be placed in the next decrease row 2015 (Hydrothermal coefficient ((HTC) (Formula 7.5) = 0.230–0.613) – 2017 (0.349–0.806) – 2016 (0.682–0.893) – 2020 (0.649–1.474) – 2019 (1.003–1.555) – 2018 (1.349–3.124).

$$HTC = \sum R \times (0.1 \times \sum t_{>10})^{-1}, \quad (5.7)$$

where ΣR – the amount of precipitation, mm over a period with temperatures above 10 ˚C; Σt > 10 ˚C – the sum of effective temperatures over the same period. According to Vlăduţ et al. (2018): HTC > 1.6 – excessive humidity, HTC 1.3–1.6 – humid conditions, HTC 1.0–1.3 – slightly arid conditions, HTC 0.7–1.0 – arid conditions, HTC 0.4–0.7 – very arid conditions.

The data obtained were analyzed using the analysis of ANOVA with determination of the share of influence of factors in the dispersion scheme (Wong, 2018). Tukey HSD Test in R (version R statistic i386 3.5.3) with a multiple comparisons of the parameter means the 99.9, 99 and 95% family-wise confidence level were used.

The object of research was oilseed radish (*Raphanus sativus* L. var. *oleiformis* (synonymous name *oleiferus*) Pers.) defined as a species of radish (*Raphanus sativus* L.), genus Raphanus L, subtribe II Raphanusae DC., tribe 5 Brassiceae Hayek and referred to the family Brassicaceae, order Capparidales, class Dicjtyledaneae (Francis et al., 2021). According to the results of some studies, it belongs to the group of species convar. oleiferus L., that is a group of varieties of oilseed radish with the following characteristics: plants are annual (95-110 days of vegetation), the taproot is not formed, it is grown to produce oil from the seeds and for forage purposes, vegetative and generative organs are similar to the forms of root crops (Tsytsiura, 2019). Oilseed radish has long been used as forage and green manure in Europe and South Africa. The proximate composition of seed in in tested varieties is shown in Tables 5.12–5.13.

Table 5.12

**The average chemical composition of the seeds of the investigated 12 varieties of oilseed radish (content in absolutely dry matter, ± standard deviation (based on the results of the multi-year assessment 2015-2020)), (%) (Tsytsiura, 2023)**

| Seeds | Moisture | Protein | Lipid | Fiber | Ash |
|---|---|---|---|---|---|
| Content (%) | 6.57 ± 1.17 | 23.6 ± 3.8 | 37.1 ± 3.5 | 17.0 ± 1.6 | 5.2 ± 1.1 |

The avarege lipid content in absolutely dry matter was 37.1 %, which is higher than among other crops. With a potential seed yield of up to 2–3.0 t $ha^{-1}$ (Tsytsiura, 2019), the possible output of oil is 650–1000 kg $ha^{-1}$.

Due to results of the chromatographic analysis (Table 5.13) it was shown that seed of all varieties of oilseed radish possess a high content of oleic (18:1) (the range of values within the studied varieties 31.95–36.28%), linoleic (18:2) 15.06-16.89%, linolenic (18:3) 12.08-14.92%, gondoic (20:1) 7.89–9.26% and erucic (22:1) (14.79–17.80) fatty acids. This corresponded to the general profile of the ratio of fatty acids in cruciferous oil. The most common among listed fatty acids in the composition seed oil of Brassicaceae plants are oleic (18:1), linoleic (18:2), linolenic (18:3), gondoic (20:1) and erucic (22:1) (Ratanapariyanuch et al., 2013). The obtained results on the structure of the identified fatty acids was similar to the previously obtained results as in the recent studies of Blume et al. (2018), Fadhil et al. (2020), Stevanato & de Silva (2019), Stevanato et al. (2020), de Mello et al. (2021) and in the earlier Domingos et al., (2008), de Andrade Ávila et al. (2012), Chammoun et al. (2013), Zhao et al. (2017).

Table 5.13

**Oil fatty acid composition of different oilseed radish (Raphanus sativus var. oleifera) varieties (content ± standard deviation (based on multi-year assessment 2015–2020)), (%) (Tsytsiura, 2023)**

| CN:DB[×] | Fatty acid / variety | 'Raiduha' | 'Zhuravka' | 'Lybid' | 'Fakel' | 'Ramonta' | 'Tambov-chanka' | 'Alpha' | 'Olga' | 'Iveya' | 'Sabina' | 'Nika' | 'Snizhana' |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| C 8:0 [××]<2e-3[*] | Octanoic [×××] (26.8) | 0.16 ± 0.05 | 0.36 ± 0.08 | 0.21 ± 0.09 | 0.11 ± 0.05 | 0.00 (trace) | 0.00 | 0.00 | 0.00 | 0.00 [*](trace) | 0.00 | 0.00 | 0.00 (trace) |
| C 11:0 *<2e-3*[*] | Undecanoic (32.4) | 0.33 ± 0.07 | 0.55 ± 0.11 | 0.18 ± 0.05 | 0.14 ± 0.04 | 0.11 ± 0.07 | 0.15 ± 0.06 | 0.00 | 0.00 | 0.00 (trace) | 0.00 | 0.00 | 0.00 (trace) |
| C 14:0 *<2e-1*[ns] | Myristoleic (22.8) | 0.07 ± 0.04 | 0.07± 0.04 | 0.08 ± 0.03 | 0.06 ± 0.05 | 0.04 ± 0.03 | 0.06 ± 0.02 | 0.06 ± 0.02 | 0.07 ± 0.01 | 0.04 ± 0.02 | 0.04 ± 0.01 | 0.05 ± 0.01 | 0.03 ± 0.01 |
| C 16:0 *<2e-4*[*] | Palmitic (18.5) | 5.11 ± 0.78 | 4.68 ± 0.89 | 5.06 ± 1.11 | 5.00 ± 1.23 | 5.02 ± 1.17 | 5.08 ± 1.09 | 5.33 ± 0.87 | 5.22 ± 0.85 | 5.12 ± 1.26 | 4.84 ± 1.41 | 4.76 ± 0.59 | 5.02 ± 0.64 |
| C 16:1 *<2e-1*[ns] | Palmitoleic (23.3) | 0.13 ± 0.03 | 0.14 ± 0.05 | 0.15 ± 0.04 | 0.15 ± 0.03 | 0.11 ± 0.04 | 0.08 ± 0.02 | 0.12 ± 0.03 | 0.10 ± 0.02 | 0.07 ± 0.02 | 0.09 ± 0.01 | 0.10 ± 0.05 | 0.12 ± 0.02 |
| C 18:0 *<2e-3*[*] | Stearic (16.9) | 2.60 ± 0.33 | 2.37 ± 0.51 | 2.46 ± 0.30 | 2.03 ± 0.44 | 2.12 ± 0.29 | 2.21 ± 0.39 | 2.24 ± 0.67 | 2.29 ± 0.55 | 2.26 ± 0.51 | 2.13 ± 0.41 | 2.11 ± 0.67 | 2.13 ± 0.59 |
| C 18:1 *<2e-3*[*] | Elaidic (17.1) | 0.08 ± 0.02 | 0.18 ± 0.05 | 0.05 ± 0.01 | 0.11 ± 0.02 | 0.14 ± 0.01 | 0.07 ± 0.02 | 0.00 | 0.00 (trace) | 0.00 | 0.00 | 0.00 (trace) | 0.00 |
| C 18:1 *<2e-3*[*] | [cis -9] Oleic (14.2) | 33.53 ± 4.38 | 33.19± 3.89 | 34.08 ± 3.55 | 31.95 ±5.14 | 31.34 ±4.89 | 33.72 ± 5.17 | 35.91 ± 4.87 | 33.59 ± 6.17 | 33.27 ± 5.91 | 34.97 ± 5.17 | 34.62 ± 4.14 | 36.28 ± 4.96 |
| C 18:2 *<2e-6*[**] | [cis -9,12] Linoleic (20.8) | 15.22 ± 3.56 | 15.53 ± 3.25 | 15.06 ± 3.24 | 16.81 ± 3.51 | 15.70 ± 4.11 | 17.08 ± 4.09 | 16.19 ± 3.77 | 16.90 ± 3.52 | 16.61 ± 3.78 | 16.89 ± 4.05 | 16.12 ± 4.26 | 16.23 ± 3.77 |
| C 18:3 *<2e-6*[**] | [cis-9, 12, 15] α-Linolenic (18.5) | 12.40 ± 2.21 | 12.08 ± 2.39 | 13.01 ± 2.49 | 13.10 ± 2.56 | 13.28 ± 2.93 | 12.26 ± 2.54 | 13.66 ± 2.49 | 13.84 ± 2.72 | 14.92 ± 2.84 | 14.42 ± 2.41 | 14.03 ± 1.98 | 12.97 ± 1.95 |
| C 20:0 *<2e-6*[**] | Arachidic (27.9) | 0.96 ± 0.17 | 0.91 ± 0.11 | 0.94 ± 0.14 | 0.66 ± 0.10 | 0.76 ± 0.20 | 0.79 ± 0.27 | 0.70 ± 0.31 | 0.72 ± 0.19 | 0.71 ± 0.23 | 0.75 ± 0.29 | 0.71 ± 0.34 | 0.63 ± 0.31 |
| C 20:1 *<2e-6*[**] | Gondoic (22.7) | 9.15 ± 2.07 | 8.48 ± 2.05 | 8.84 ± 2.03 | 9.12 ± 1.99 | 8.92 ± 1.84 | 8.55 ± 1.77 | 8.12 ± 1.71 | 8.06 ± 1.92 | 7.92 ± 1.87 | 7.89 ± 2.19 | 9.14 ± 2.29 | 9.26 ± 1.67 |
| C 20:2 *<2e-5*[**] | [cis -11, 14] Eicosadienoic(32.6) | 0.47 ± 0.14 | 0.39 ± 0.17 | 0.26 ± 0.14 | 0.28 ± 0.12 | 0.40 ± 0.15 | 0.28 ± 0.10 | 0.33 ± 0.09 | 0.41 ± 0.11 | 0.21 ± 0.08 | 0.32 ± 0.11 | 0.20 ± 0.14 | 0.24 ± 0.09 |

(End of Table 5.13)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C 20:3 <2e-3* | Eicosatrienoic (25.2) | 0.13 ± 0.06 | 0.12 ± 0.04 | 0.10 ± 0.02 | 0.10 ± 0.03 | 0.12 ± 0.03 | 0.08 ± 0.02 | 0.15 ± 0.03 | 0.13 ± 0.03 | 0.08 ± 0.03 | 0.07 ± 0.03 | 0.05 ± 0.01 | 0.08 ± 0.03 |
| C 20:4 <2e-3* | Arachidonic (24.5) | 0.12 ± 0.03 | 0.14 ± 0.02 | 0.14 ± 0.03 | 0.12 ± 0.04 | 0.13 ± 0.05 | 0.15 ± 0.02 | 0.10 ± 0.03 | 0.11 ± 0.03 | 0.10 ± 0.04 | 0.05 ± 0.01 | 0.05 ± 0.02 | 0.07 ± 0.02 |
| C 20:5 <2e-7** | [cis -5, 8, 11, 14, 17] Eicosapen-taenoic (21.7) | 1.24 ± 0.27 | 1.11 ± 0.22 | 1.08 ± 0.31 | 1.02 ± 0.24 | 1.37 ± 0.29 | 0.97 ± 0.23 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 (trace) | 0.00 (trace) |
| C 21:0 <2e-4* | Geneicosanoic (28.3) | 0.00 (trace) | 0.46 ± 0.09 | 0.00 (trace) | 0.00 (trace) | 0.00 | 0.36 ± 0.07 | 0.00 | 0.44 ± 0.13 | 0.39 ± 0.10 | 0.32 ± 0.12 | 0.00 (trace) | 0.33 ± 0.09 |
| C 22:0 <2e-7** | Behenic (29.8) | 0.37 ± 0.11 | 0.41 ± 0.07 | 0.39 ± 0.14 | 0.08 ± 0.03 | 0.28 ± 0.10 | 0.07 ± 0.02 | 0.32 ± 0.12 | 0.24 ± 0.09 | 0.30 ± 0.12 | 0.00 (trace) | 0.31 ± 0.07 | 0.00 (trace) |
| C 22:1 <2e-7** | [cis -13] Erucic (17.9) | 15.20 ± 2.07 | 15.95 ± 2.18 | 15.93 ± 2.79 | 16.70 ± 2.56 | 17.80 ± 2.75 | 15.59 ± 2.92 | 17.66 ± 3.02 | 15.74 ± 3.09 | 16.18 ± 2.93 | 15.73 ± 2.38 | 16.30 ± 2.49 | 14.79 ± 2.37 |
| C 22:2 <2e-6** | [cis -13, 16] Docosadienoic (26.7) | 0.38 ± 0.09 | 0.51 ± 0.12 | 0.25 ± 0.09 | 0.27 ± 0.08 | 0.15 ± 0.04 | 0.17 ± 0.05 | 0.12 ± 0.03 | 0.14 ± 0.04 | 0.17 ± 0.04 | 0.11 ± 0.05 | 0.10 ± 0.03 | 0.12 ± 0.04 |
| C 23:0 <2e-4* | Tricosanoic (27.5) | 0.45 ± 0.14 | 0.42 ± 0.12 | 0.41 ± 0.09 | 0.39 ± 0.17 | 0.42 ± 0.11 | 0.42 ± 0.08 | 0.47 ± 0.09 | 0.44 ± 0.07 | 0.46 ± 0.08 | 0.43 ± 0.12 | 0.39 ± 0.08 | 0.46 ± 0.17 |
| C 24:0 <2e-4* | Lignoceric (28.1) | 0.44 ± 0.24 | 0.52 ± 0.27 | 0.31 ± 0.11 | 0.39 ± 0.18 | 0.57 ± 0.17 | 0.14 ± 0.05 | 0.34 ± 0.16 | 0.34 ± 0.14 | 0.45 ± 0.09 | 0.33 ± 0.11 | 0.38 ± 0.14 | 0.41 ± 0.24 |
| C 24:1 <2e-10*** | Nervonic (34.9) | 1.46 ± 0.36 | 1.43 ± 0.34 | 1.01 ± 0.28 | 1.41 ± 0.50 | 1.22 ± 0.42 | 1.72 ± 0.48 | 1.18 ± 0.51 | 1.22 ± 0.39 | 0.74 ± 0.30 | 0.62 ± 0.28 | 0.58 ± 0.24 | 0.83 ± 0.33 |
| Total | | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Total saturated | | 11.34 | 11.65 | 10.55 | 9.41 | 9.87 | 9.73 | 9.91 | 10.31 | 10.11 | 9.27 | 9.01 | 9.37 |
| Monounsaturated | | 59.55 | 59.37 | 60.06 | 59.44 | 59.53 | 59.73 | 59.99 | 58.71 | 58.18 | 59.30 | 60.74 | 61.28 |
| Polyunsaturated | | 29.11 | 28.98 | 29.39 | 31.15 | 30.60 | 30.54 | 30.10 | 30.98 | 31.71 | 31.43 | 30.25 | 29.35 |
| Total unsaturated | | 88.66 | 88.35 | 89.45 | 90.59 | 90.13 | 90.27 | 90.09 | 89.69 | 89.89 | 90.73 | 90.99 | 90.63 |
| ER | | 0.285 | 0.286 | 0.285 | 0.294 | 0.306 | 0.277 | 0.257 | 0.270 | 0.271 | 0.263 | 0.282 | 0.269 |
| DR | | 0.323 | 0.323 | 0.323 | 0.341 | 0.332 | 0.336 | 0.337 | 0.349 | 0.355 | 0.348 | 0.334 | 0.326 |
| ODR | | 0.451 | 0.453 | 0.451 | 0.483 | 0.479 | 0.465 | 0.454 | 0.478 | 0.487 | 0.472 | 0.465 | 0.446 |
| LDR | | 0.449 | 0.438 | 0.463 | 0.438 | 0.458 | 0.418 | 0.458 | 0.450 | 0.473 | 0.461 | 0.465 | 0.444 |
| S/U | | 0.128 | 0.132 | 0.118 | 0.104 | 0.110 | 0.108 | 0.110 | 0.115 | 0.112 | 0.102 | 0.099 | 0.103 |
| PU/MU | | 0.489 | 0.488 | 0.489 | 0.524 | 0.514 | 0.511 | 0.502 | 0.528 | 0.545 | 0.530 | 0.498 | 0.479 |

*trace – the concentration was less 0.01%; ×– Carbon number (CN) per double bond (DB); ×× – level Pr(>F) for a given fatty acid to compare between oilseed varieties (Tukey HSD Test results, signifscant codes: '***' 0.001 '**' 0.01 '*' 0.05 'ns' nonsignificant); ××× – the average share of the influence of hydrothermal conditions of vegetation (%) on the amount of fatt acid content in the two-factor ANOVA system (A – year conditions, B – variety with an assessment of the content of the corresponding fatty acid).

The obtained structure of the fatty acid composition is closest to the results of Blume et al. (2018) and Domingos et al. (2008). However, the obtained data give reason to note a number of features that was different from the results obtained in the specified studies. In particular, the significance of the differences in the concentration of fatty acids within the varieties of different ecological and geographical origin in the presence of a wider spectrum of cis-isomers of fatty acids was established. According to Singer et al. (2016) this type of formation of the structure of fatty acids indicated the high-amplitude nature of temperature and moisture during the period of seed formation and filling. At the same time, the difference is proven statistically. The level of significance for the majority of fatty acids (linoleic, α-linolenic, arachidic, gondoic, eicosadienoic, eicosapentaenoic, behenic, erucic, docosadienoic) in the comparison of oilseed radish varieties is $p<0.01$. For nervonic fatty acid, this level was $p <0.001$, and for myristoleic and palmitoleic fatty acids, the differences in the content of varieties were insignificant. For the rest of the fatty acids, the significance of differences between varieties was $p<0.05$. Among the full list of the identified composition, no such acid as octanoic (8:0) was detected in 5 varieties, in 4 varieties such acids as undecanoic (11:0), elaidic (18:1) and eicosapentaenoic (20:5) were found in two varieties of fatty geneicosanoic acid (21:0). At the same time, these same acids were not identified for oil radish in the same studies by Blume et al. (2018) and Domingos et al. (2008). Such results allow us to ascertain a wider range of fatty acids in the composition of oilseed radish than was noted and to form a classification of varieties according to the suitability of its oil for biofuel use.

The variability of the values of the concentration of the corresponding fatty acids by the value of the presented standard deviation was ranked for varieties in the range from 7.6 to 53.7%. Variability was due to both annual variance and internal variability within the limits of the obtained results of four-fold repetition of determinations, taking into account the general error of the experiment. The level of variation was consistent with the generalization results of Velasco et al. (1998), Mendal et al. (2002), de Andrade Ávila et al. (2012), Wendlinger et al. (2014). It should be noted that according to the amino acid composition of other cruciferous crops (statistical long-term data according to Giakoumis (2018)), in terms of dominant fatty acids, oil of oilseed radish contains (as a percentage of comparison with the concentration) myristoleic fatty acid by 25% more than in rapeseed, spring bittercress, camelina and red by 42.9% more than in white mustard. The content of oleic fatty acid is 43.0% lower than that of rapeseed and 26.9% lower than that of spring bittercress, but 17.6% higher than that of white mustard and 1.5 times higher than that of camelina. In terms of erucic acid content in radish oil was second only to white mustard (40.1% reduction). The content of linoleic fatty acid is less than 7.3% in comparison with camelina and 16.6% and 21.8%, respectively, less in rapeseed and spring bittercress, and greater by 14.3% less than in white mustard. The content of linolenic fatty acid is 1.8 times more than that of rapeseed and 50.0% more than that of spring bittercress, but on the same level with white mustard and 55.7% less than camelina.

In addition, the share of the influence of hydrothermal conditions of the vegetation of oilseed radish on the structure of the fatty acid composition of its oil was determined in the dispersion scheme of year-variety-relevant fatty acid-random (not account) factors. The influence value thus obtained ranged from 16.9% for stearic fatty acid to 34.9% for nervonic fatty acid. The determined nature of the effect allows to evaluate the components of the fatty acid composition of the oil for plasticity and stability and in the future to predict the approximate fatty acid composition of the oil of this variety based on its genotypically characteristic structure and weather conditions during the period of seed formation.

According to the chemical structure of the fatty acid composition, the ratio of saturated and unsaturated fatty acids in all studied varieties had a small interval ratio of 9.01–11.65:88.35–90.99 (%). Among the unsaturated fatty acids, monounsaturated fatty acids prevailed with the average value for varieties according to their ratio to polyunsaturated as 59.69:30.34 (%) with an average share of saturated 9.97%. The established differences in the fatty acid composition led to a corresponding spread of values according to the main fatty acid ratios (Formulas 5.1–5.6). Thus, Blume et al. (2018) indicate that very large amount of polyunsaturated fatty acids will significantly reduce oxidative stability of obtained fuel and oil presents a mixture had a large number of different fatty acids. For this reason, some coefficients are usefull for more accurate assessment of the qualitative composition of different oil types: ER (elongation ratio), DR (desaturation ratio), ODR (oleic desaturation ratio), LDR (linoleic desaturation ratio). Mentioned ratios show relation between different groups of fatty acids with similar properties and probably could show activity of respective desaturase or elongase (Atabani et al., 2013). It is indicated (Blume et al. (2018)) that biodiesel fuel could be divided into two groups: heavy and light (which could be used as additive to aviation fuel) type of fuel according to length of carbon chain. The biggest difficulty of fatty acid composition assessment is large number of various fatty acids, each of which has specific properties. Obtained fuel from certain types of oil should have small carbon number (preferably not more than 18), therefore important is the contents of the mono- and polyunsaturated fatty acids with short chain (such as C 18:2, C 18:3). On the other hand very large amount of polyunsaturated fatty acids will significantly reduce oxidative stability of obtained fuel (Firestone, 2013). Also to assess the results of the chromatographic analysis used as indicators S/U (saturated fatty acids/unsaturated fatty acids) and PU/MU (polyunsaturated fatty acids/monounsaturated fatty acids) proportions (Blume et al., 2018). At the same time, in the practice of evaluating oils for biofuel (Clancy, 2013; Shah et al., 2013; Faria et al., 2018), preference should be given to oils with a high content of unsaturated fatty acids (primarily monounsaturated) and also the lowest value such fatty acid ratios PU/MU, ER DR. The highest index of LDR value has been found due to the highest content of linolenic acid (C18:3) what could indicate reduced oxidative stability (Blume et al., 2018).

According to the indicated dataset and considering as the resulting indicator PU/MU (Fadhil et al., 2020), the investigated varieties of oilseed radish can be placed in the following order of increasing suitability of its oil as a biofuel component: ‘Zhuravka’ – ‘Raiduha’ – ‘Lybid’ – ‘Olga’ –’Iveya’ – ‘Ramonta’ – ‘Alpha’ – ‘Tambovchanka’ – ‘Fakel’ – ‘Snizhana’ – ‘Sabina’ – ‘Nika’. It should also be noted that the high content of erucic fatty acid 14.80-17.80% allowed to classify this oil as not suitable for food purposes and determined the importance of its application for bioenergetic. The results of the oil fatty acid composition were confirmed by the clustering (Figure 5.3).

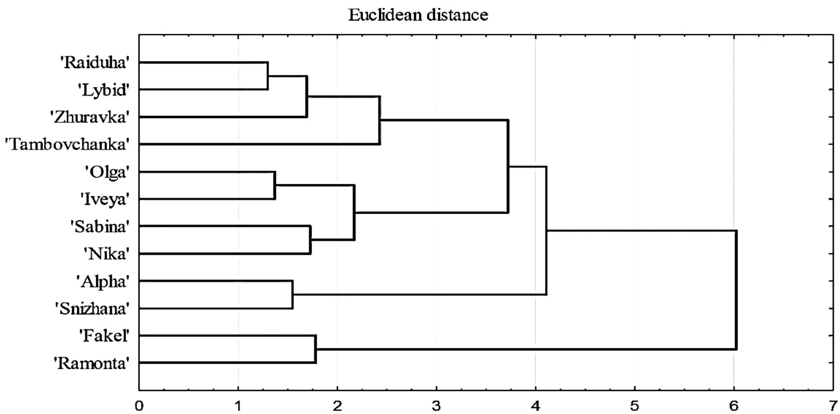



**Figure 5.3 – Cluster analysis of 12 oilseed radish varieties by fatty acid content in its oil (full linkage method for the 2015-2020 dataset) (Tsytsiura, 2023)**

This cluster confirmed the significance of the difference between the studied varieties in the concentration of individual fatty acids according to the seven groups of Euclidean distances determined in the clustering of data according to the full linkage method scheme. It also indicated the proximity of varieties were in neighboring positions in a certain range of suitability of its oil for biofuel use. That was confirmed the reliability of the conducted ranking of varieties.

It is noted (Mat et al., 2020) the importance, together with the study of the fatty acid composition of the oil, of the assessment of its physical and physicochemical constants. The data of such assessment are presented in Table 3. The values of the presented groups of indicators correspond to the defined interval indicators for oil in the species category 'Fodder radish crude oil' (CERBIO, 2007; de Andrade Ávila, 2013; Clancy, 2013; Ratanapariyanuch et al., 2013; Faria et al., 2018). According to the specified parameters, the oil from oilseed radish varieties under ordinary cold pressing belongs to the group of semi-drying oils. In comparison to a number of vegetable oils (the first 7 was most widely used in biofuel practice in the research region, and jatropha oil is gaining popularity (Riayatsyah et al., 2022)), oil from oil radish should be classified as suitable for biofuel use by basic parameters. This is confirmed by both the comparison and the conclusions of a number of studies (de Andrade Ávila, 2013; Clancy, 2013; Blume et al., 2018; Fadhil et al., 2020; Paricaud et al., 2020). The positive aspects of this oil include a high calorific value of combustion (one of the highest among cruciferous oils), a relatively low percentage of carbon residue, which is 0.07-0.20% lower than that of traditional rapeseed and soybean oils. The last factor was positive in view of the predicted using of fuel equipment. The negative aspects included high acidity and lower values of the 'solidification temperature' indicator against the background of a significantly higher value of the flash point (265 °C). The interaction of these factors in view of the research of Giakoumis (2018) and Paricaud et al. (2020) limits its use in a single-component version even with the addition of corrective organic additives (Domingos et al., 2008). According to the presented data, it is expedient to use this oil in the variant of combined use of mixed biofuels. At the same time, the optimal version of the mixtures should be investigated in detail, despite a certain reciped recommendation in practice with the participation of oilseed radish oil (Pedro et al., 2009; de Andrade Ávila et al., 2012; Clancy, 2013; Faria et al., 2018; Fadhil et al., 2019). This was confirmed by the results of changes in the basic physical and physicochemical parameters of radish oil during the polymerization and oxypolymerization process (Tables 5.14–5.15). Due to the polymerization of the oil at a temperature of 280 °C, which corresponded to the maximum possible level of the flash point of the oil and its heating in combination with oxypolymerization, it was possible to study changes in the physical and physico-chemical parameters of the oil under conditions close to the conditions in the fuel supply system and its preparation before injection into the combustion chamber of the engine.

Considering the results of research by Dahmen & Marquardt (2017), Tucki et al. (2019) the behavior of oil from oil radish under the combination of oxypolymerization and constant heating modes can be assessed as stable. Both modes of oxypolymerization at temperatures of 120°C and 150°C showed similar changes in the specific gravity of the oil. Moreover, long-term heating increased this indicator to control ($p<0.05$) only in the option of heating for 2 and 3 hours. The absence of the previous oxypolymerization process increased the reaction sensitivity of the oil to long-term heating during the polymerization process, which led to a significant ($p<0.05$)

indicator of the specific density of the oil already in the option of heating for one hour.

On the contrary, the refractive index had more significant changes in the heating variants of pre-oxypolymerized oil. Oxypolymerization was also positively reflected on the basic indicators of acid, iodine, ether numbers and saponification number. Significant changes in the full set of these parameters ($p<0.05...0.01$) were noted only in the variant of preliminary oxypolymerization at 150 °C with heating for 2 and 3 hours. The oil without prior oxypolymerization had more significant changes ($p<0.01...0.001$) in terms of the basic indicators of the physicochemical properties of the oil compared to the control, especially in the heating option for 3 hours.

The obtained results confirmed the suitability of oil from oilseed radish for thermodynamic combustion processes in regulated pressure and temperature systems. Such results are consistent with the data of Chammoun (2013), Ratanapariyanuch (2013) and Faria et al. (2018).

However, these conclusions are based not only on the analysis of the chemical composition of the oil itself, but also take into account certain transformation processes that the oil undergoes during its stay in the fuel system of a heated engine.

Based on the comparison of the oil from the seeds of oilseed radish varieties of different breeding both in terms of the structure of the fatty acid composition and its physical and physico-chemical properties, this crop should be considered as one of the promising ones for use in the production of multicomponent biofuels. Oil from these varieties on average is characterized by high content of monounsaturated (59.69%) fatty acids, especially the highest value of oleic (18:1) acid (33.87%).

Polyunsaturated/monounsaturated fatty acid ratio (PU/MU) was rather lower – 0.479–0.545, so oxidative stability of this oil was high. The other fatty acid ratios (desaturation ratio (DR) – 0.326–0.349, elongation ratio (ER) – 0.257–0.306, oleic desaturation ratio (ODR) – 0.446–0.487, linoleic desaturation ratio (LDR) – 0.418–0.473, saturated/unsaturated (S/U) – 0.099–0.132) indicate a wide range of potential biofuel use of the oil of this plant species. Particularly valuable in this regard was the varieties of ‘Sabina’ and ‘Nika’ with the highest value of oleic (18:1) acid (34.62–34.97%) with an S/U ratio of 0.099–0.102.

Table 5.14

**Average values of physical and physicochemical indicators of oil for 12 varieties of oilseed radish (*Raphanus sativus* var. *oleifera*) (± standard deviation (2015–2020)) and the range of its values for oils of other crops (Tsytsiura, 2023)**

| Sample of oil | Organoleptic properties | | | | |
|---|---|---|---|---|---|
| | **colour (Lovibond, 1 in.)** | **transparency** | **colour (iodine scale)** | **odor** | **taste** |
| Cold pressed oil | Y25.00, R2.00 – Y35.00, R2.60 | absolute transparency after 24 hours | 30-40 | light radish hue | soft, satisfying with a radish taste |

| Physical indicators | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| density at 20 °C, kg $m^{-3}$ | refractive index at 20 °C, | rotation of the plane of polarization at 23 °C, ° | specific viscosity at 20 °C, $mm^2 s^{-1}$ | kinematic viscosity of oil at 20°C $mm^2 s^{-1}$ | relative surface tension | carbon residue (wt.%) | net calorific value, MJ $kg^{-1}$ | solidification temperature,°C | flash point, °C | solubility in organic solventsdensity |
| 0.912 ± 0.047 | 1.468 ± 0.012 | -0.73 ± 0.02 | 70.39 ± 0.58 | 77.18 ± 0.55 | 0.459 ± 0.011 | 0.31 ± 0.12 | 37.93 ± 0.29 | -11.5 ± 2.0 | 265.0 ± 23.7 | Well soluble |

| Chemical indicators | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| acid value, mg KOH $g^{-1}$ | content of free acids in % of oleic acid | saponification value, mg KOH $g^{-1}$ | ether value, mg KOH $g^{-1}$ | iodine value, g $I_2$ $(100 \cdot g)^{-1}$ | rhodan value, g $(SCN)_2$ $(100 \cdot g)^{-1}$ | amount of water-insoluble fatty acids (gener number) | amount of unsaponifiable matter, % | sulfur content (wt.%) |
| 3.80 ± 0.30 | 0.45 ± 0.10 | 170.0 ± 1.8 | 168.4 ± 2.1 | 104.8 ± 2.4 | 81.4 ± 1.5 | 92.2 ± 1.8 | 1.17 ± 0.15 | 0.0017 ± 0.005 |

(End of Table 5.14)

| Range of observed values of indicators in various studies for the period 1950–2018 based on Firestone (2013), Tsytsiura & Tsytsiura (2015), Giakoumis (2018) | Rapeseed (*Brassica napus* subsp. Napus) | White mustard (*Sinapis alba* L) | Spring bittercress (*Brassica campestris* var. *oleifera* f *annua* D.C) | Camelina (*Camelina sativa* (L.) Crantz) | Safflower (*Carthamus tinctorius* L) | Soybean (*Glycine max* (L) Merrill) | Linseed (*Linum usitatissimum* L. var. *intermedia*) | Jatropha (*Jatropha curcas* L.) |
|---|---|---|---|---|---|---|---|---|
| Kinematic viscosity of oil at 20°C, $mm^2 s^{-1}$/ | 74.6–77.2 | 66.6–69.7 | 75.8–78.4 | 51.2–53.4 | 65.8–68.4 | 56.9–57.8 | 60.8–62.9 | 57.8–61.3 |
| Acid value | 0.1–11.0 | 0.06–8.5 | 0.8–7.3 | 0.5–5.0 | 0.8–5.8 | 0.0–5.7 | 0.5–1.5 | 8.7–9.8 |
| Iodine value | 95–118 | 79–115 | 105–122 | 133–155 | 138–155 | 120–141 | 175–204 | 98–103 |
| Flash point, °C | 255.4–276.1 | 238.7–257.2 | 245.9–264.7 | 183.7–218.5 | 246.9–277.3 | 230.7–254.4 | 220.4–249.8 | 232.8–247.5 |
| Solidification temperature,°C | 0.0… –10.0 | –8.0… –16.0 | –6.0… –8.0 | –14.0… –16.0 | –8.0… –16.0 | –10.0… –18.0 | –16.0... –27.0 | 0.5… 1.0 |
| Carbon residue (wt.%) | 0.38–0.51 | 0.33–0.46 | 0.39–0.55 | 0.24–0.32 | 0.42–0.67 | 0.44–0.69 | 0.27–0.41 | 0.47–0.72 |
| Net calorific value, $MJ\ kg^{-1}$ | 37.1–40.2 | 36.4–38.2 | 36.8–37.2 | 36.5–37.0 | 36.4–37.0 | 37.0–37.6 | 36.7–37.0 | 36.7–37.2 |

Table 5.15

**Changes in the physicochemical parameters of oxypolymerized and unoxypolymerized oil of 'Zhuravka' variety in the process of its temperature polymerization (heating at 280 °C (average value for 4 years of study 2017–2020 (± standard deviation)) (Tsytsiura, 2023)**

| Variant | Heating, hours | Density at 20 °C, kg m$^{-3}$ | Refractive index | Acid value | Content of free acids in % of oleic acid | Saponification value | Ether n value | Iodine value |
|---|---|---|---|---|---|---|---|---|
| Control variant (heated oil) | - | $0.913 \pm 0.058$ | $1.471 \pm 0.001$ | $3.75 \pm 0.50$ | $2.10 \pm 0.55$ | $181.15 \pm 2.84$ | $175.52 \pm 7.35$ | $108.52 \pm 2.33$ |
| Heated oil without oxypolymerization up to 120°C | 1 | $0.928^{c*} \pm 0.041$ | $1.472^{ns} \pm 0.002$ | $18.30^{a} \pm 1.35$ | $9.05^{a} \pm 2.15$ | $186.08^{c} \pm 3.52$ | $170.43^{c} \pm 6.51$ | $93.09^{b} \pm 3.45$ |
| | 2 | $0.931^{c} \pm 0.044$ | $1.473^{c} \pm 0.003$ | $25.10^{a} \pm 1.52$ | $12.55^{a} \pm 2.30$ | $189.42^{c} \pm 3.85$ | $167.55^{b} \pm 5.44$ | $82.82^{a} \pm 2.64$ |
| | 3 | $0.935^{b} \pm 0.051$ | $1.474^{c} \pm 0.002$ | $27.95^{a} \pm 1.60$ | $14.20^{a} \pm 2.70$ | $188.21^{c} \pm 2.15$ | $157.71^{a} \pm 3.62$ | $71.72^{a} \pm 3.52$ |
| Oxypolymerized oil at temperature 120 °C | 1 | $0.917^{ns} \pm 0.035$ | $1.473^{c} \pm 0.002$ | $3.50^{c} \pm 1.78$ | $1.74^{c} \pm 0.16$ | $177.89^{ns} \pm 1.53$ | $175.22^{ns} \pm 4.10$ | $105.85^{ns} \pm 2.83$ |
| | 2 | $0.924^{c} \pm 0.041$ | $1.474^{c} \pm 0.002$ | $3.65^{ns} \pm 1.92$ | $1.82^{c} \pm 0.18$ | $180.05^{ns} \pm 3.20$ | $175.59^{ns} \pm 4.52$ | $97.83^{b} \pm 3.15$ |
| | 3 | $0.924^{c} \pm 0.052$ | $1.474^{c} \pm 0.002$ | $3.79^{c} \pm 1.87$ | $1.87^{c} \pm 0.14$ | $181.55^{ns} \pm 2.58$ | $176.89^{ns} \pm 3.57$ | $97.47^{b} \pm 2.81$ |
| Oxypolymerized oil at temperature 150 °C | 1 | $0.914^{ns} \pm 0.036$ | $1.473^{c} \pm 0.002$ | $3.40^{c} \pm 1.72$ | $1.75^{c} \pm 0.21$ | $179.14^{ns} \pm 3.05$ | $174.85^{ns} \pm 3.89$ | $103.92^{c} \pm 3.92$ |
| | 2 | $0.920^{c} \pm 0.053$ | $1.473^{c} \pm 0.003$ | $3.48^{c} \pm 1.88$ | $1.72^{c} \pm 0.28$ | $181.53^{ns} \pm 3.28$ | $178.15^{c} \pm 4.18$ | $92.56^{b} \pm 4.09$ |
| | 3 | $0.927^{c} \pm 0.067$ | $1.475^{b} \pm 0.004$ | $3.59^{c} \pm 1.97$ | $1.74^{c} \pm 0.37$ | $183.12^{ns} \pm 3.91$ | $179.58^{c} \pm 4.63$ | $91.72^{b} \pm 4.56$ |
| level *Pr(>F)* for the Tukey HSD Test | | *<2e-3** | *<2e-2** | *<2e-3** | *<2e-6*** | ≈ ns | *<2e-2** | <2e-7** |

*–letter indexing for the appropriate confidence level (in comparison to the control variant): a'***' 0.001; b'**' 0.01; c '*' 0.05; ns (nonsignificant).

The possibility of successful use of oil from oilseed radish is also confirmed on the basis of a comparative analysis of its basic properties with other oils common in biofuel production. Among the valuable features, a low level of carbon residue (0.31 wt.%) and low sulfur content (0.0017 wt.%), a high level of calorific value (37.93 MJ $kg^{-1}$), preservation of the main physical and physico-chemical parameters of the oil during high-temperature flow (polymerization) especially against the background of its oxypolymerization. The last factor confirms the possibility of successful use of this oil in closed engine systems. However, low freezing point and high flash point, higher values of its viscosity give reasons to recommend its use in the format as a component of mixed biofuels. This direction needs additional scientific study.

The results of such studies, including chromatographic analysis of radish oil for composition and content of higher fatty acids (HFAs) are shown in Table 5.16.

Table 5.16

**Content and composition of higher fatty acids of radish oil (Ukhanov, 2018)**

| Fatty acid | Formula | Content in radish oil, % |
|---|---|---|
| 1 | 2 | 3 |
| *Saturated, including:* | | 9.372 |
| Myristic | $C_4H_{28}O_2$ | 0.046 |
| Pentadecane | $C_{15}H_{30}O_2$ | 0.018 |
| Palmitic | $C_{16}H_{32}O_2$ | 5.107 |
| Stearic | $C_{18}H_{36}O_2$ | 2.458 |
| Arachinic | $C_{20}H_{40}O_2$ | 0.893 |
| Behenic | $C_{22}H_{44}O_2$ | 0.403 |
| Lignoceric | $C_{24}H_{48}O_2$ | 0.511 |
| *Monounsaturated, including:* | | 55,159 |
| Palmitooleic | $C_{16}H_{30}O_2$ | 0.114 |
| Oleic | $C_{18}H_{34}O_2$ | 32.194 |
| Gondoic | $C_{20}H_{38}O_2$ | 9.155 |
| Erucic | $C_{22}H_{42}O_2$ | 12.517 |
| Nervonic | $C_{24}H_{46}O_2$ | 1.179 |
| *Polyunsaturated, including:* | | 35,408 |
| Linoleic | $C_{18}H_{32}O_2$ | 22.015 |
| Eicosadiene | $C_{20}H_{36}O_2$ | 0.424 |

(End of Table 5.16)

| 1 | 2 | 3 |
|---|---|---|
| Docosadiene | $C_{22}H_{40}O_2$ | 0.024 |
| u-linolenic | $C_{18}H_{30}O_2$ | - |
| a-linolenic | $C_{18}H_{30}O_2$ | 12.800 |
| Docosatrienoic | $C_{22}H_{38}O_2$ | 0.030 |
| Stearidonic | $C_{18}H_{28}O_2$ | - |
| Arachidonic | $C_{20}H_{32}O_2$ | 0.115 |

The total content of monounsaturated HFAs was 55.2%, polyunsaturated 35.4%, and saturated acids 9.4%.

The content of erucic acid 12.5%, oleic acid 32.2%, linoleic acid 22% and a-linolenic acid 12.8% were high in radish oil.

Evaluation of the effect of commercial mineral diesel fuel additive on the ratio of higher fatty acids in blended radish-mineral fuels

Blended fuel with different content of commercial mineral diesel fuel in the radish oil on the ratio of higher fatty acids (HFA) was investigated to determine the extent of the effect of addition of commercial mineral diesel fuel to radish oil on the ratio of higher fatty acids (HFA). The addition of mineral diesel fuel to the cutting oil resulted in a slight change in the ratio of HFAs in the vegetable oil (Table 5.17).

Table 5.17

**Effect of commercial mineral diesel fuel additive on the relative content of HFCs in radish oil and blended radish-mineral fuel (Ukhanov, 2018)**

| Fatty acid | Relative content,% | | | | | $LSD_{05}$ |
|---|---|---|---|---|---|---|
| | Share of oil in the mixture, % | | | | | |
| | 100 | 90 | 75 | 50 | 25 | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Myristic | 0.046 | 0.034 | 0.028 | 0.022 | 0.021 | 0.004 |
| Pentadecane | 0.018 | 0.144 | 0.332 | 0.985 | 1.975 | 0.017 |
| Palmitic | 5.107 | 5.088 | 5.068 | 5.078 | 5.085 | 0.054 |
| Palmitooleic | 0.114 | 0.131 | 0.145 | 0.193 | 0.265 | 0.017 |
| Stearic | 2.458 | 2.381 | 2.403 | 2.290 | 2.189 | 0.032 |
| Oleic | 32.194 | 32.144 | 32.040 | 31.005 | 31.226 | 0.222 |
| Linoleic | 22.015 | 21.937 | 21.935 | 22.201 | 21.420 | 0.134 |

(End of Table 5.17)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| Y-linolenic | - | - | 0.009 | 0.022 | 0.022 | 0.003 |
| a-linolenic | 12.800 | 12.888 | 12.775 | 12.915 | 12.410 | 0.148 |
| Arachinoic | 0.893 | 0.902 | 0.905 | 0.914 | 0.885 | 0.014 |
| Gondoic | 9.155 | 9.016 | 9.091 | 8.928 | 8.866 | 0.203 |
| Eicosadiene | 0.424 | 0.454 | 0.473 | 0.610 | 0.628 | 0.031 |
| Arachidonic | 0.115 | 0.124 | 0.113 | 0.147 | 0.120 | 0.006 |
| Behenoic | 0.403 | 0.408 | 0.421 | 0.462 | 0.503 | 0.012 |
| Erucic | 12.517 | 12.546 | 12.512 | 12.435 | 12.560 | 0.154 |
| Docosadiene | 0.024 | 0.022 | 0.014 | 0.008 | 0.081 | 0.009 |
| Docosatrienoic | 0.030 | 0.026 | 0.027 | 0.022 | 0.031 | 0.009 |
| Lignoceric | 0.511 | 0.527 | 0.481 | 0.542 | 0.481 | 0.023 |
| Nervonic | 1.179 | 1.234 | 1.232 | 1.225 | 1.238 | 0.026 |

Significant increase in the content of pentadecanoic, palmy-toleic and behenic acids was observed when radish oil was mixed with commercial mineral fuel. A significant decrease in the content of linoleic, gondoic and arachinic acids was also noted.

In addition, it was noted that with increasing the proportion of mineral fuel in DCT, a decrease in the total content of HFAs with 14, 15 and 18 carbon atoms in the chain and an increase in the total content of HFAs with 22 and 24 carbon atoms in the chain was observed.

Vegetable oil obtained from radish is a mixture of mono-, di- and triacylglycerols containing higher aliphatic acids, i.e. high molecular weight acid-containing compounds with a hydrocarbon base linked to the glycerol molecule.

To determine the molecular composition of radish oil and its lower heat of combustion, the following input data are required: the number of carbon, hydrogen and oxygen atoms in the molecule of each acid, the molecular weight of the acids, and the percentage of each acid in the radish oil.

Determination of elemental composition and lower heating value of radish oil and DST was carried out using the following methodology (in full author's calculation text for Ukhanov (2018)). Knowing the percentage content (r) of higher aliphatic acids and the number of atoms (x) of carbon, (y) hydrogen and (z) oxygen in each acid CxHyOz, we determine the average number of atoms of each element in natural radish oil using the formulas:

$$x_{av} = \Sigma x_i \cdot r_i \;;\; y_{av} = \Sigma y_i \cdot r_i ;\; z_{av} = \Sigma z_i \cdot r_i . \qquad (5.8)$$

Врезультатерасчета(безучетачислаатомовнеидентифицированного остатка) получаем:

$$x_{av} = 14\cdot 0.0004+15\cdot 0.0002+16\cdot (0.0510+0.0011)+18\cdot (0.0246+0.3216+ +0.2199+0.00001+0.1282)+20\cdot (0.0089+0.0914+0.0042+0.0012)+ +22\cdot (0.0040+0.1250+0.0015+0.0068)+24\cdot (0.0103+0.0000) = 18.73;$$

$$y_{av} = 28\cdot 0.0004+30\cdot 0.0002+32\cdot 0.0510+30\cdot 0.0011+36\cdot 0.0246+ +34\cdot 0.3216++32\cdot (0.2199+0.00001)+34\cdot 0.1282+36\cdot (0.0089+0.0914)+ +38\cdot (0.0042+0.0012)+40\cdot (0.0040+0.1250)+42\cdot 0.0015+44\cdot 0.0068+ +46\cdot 0.0103+48\cdot 0.0000 = 34.71;$$

$$z_{av}=2\cdot (0.0004+0.0002+0.0510+0.0011+0.0246+0.3216+0.2199+ +0.00001+0.1282+0.0089+0.0914+0.0042+0.0012+0.0040+0.1250+ +0.0015+0.0068+0.0103+0.00) = 2.00.$$

Then the average chemical formula of the isolated acids of the radish oil will be $C_{18.73}H_{34.71}O_2$.

The author of the study (Ukhanov, 2018) determined the average molecular formula of radish oil:

$$3C_{18,73}H_{34,71}O_2+C_3H_5(OH)_3 -_3H_2O=_3C_{18.73}H_{34.71}O_2+C_3H_2.$$

Average molecular formula of radish oil $C_{59.19}H_{106.13}O_6$

Total molecular weights of each of the elements in radish oil:

$$\Sigma M(C) = M(C)\cdot x_{av} = 12.011\cdot 59.19 = 710.931 \text{ g mol}^{-1};$$

$$\Sigma M(H) = M(H)\cdot y_{av} = 1.0079\cdot 106.13 = 106.968 \text{ g mol}^{-1};$$

$$\Sigma M(O) = M(O)\cdot z_{av} = 15.9994\cdot 6 = 95.996 \text{ g mol}^{-1}.$$

The average molecular weight of radish oil was determined by the formula

$$MOSRO = \Sigma M(C) + \Sigma M(H)+ \Sigma M(O)$$

$$MOSRO = 710,931 + 106,968 + 95,996 = 913,895 \text{ g mol}^{-1}.$$

Divide the total molecular weight values of all the carbon (C), hydrogen (H) and oxygen (O) atoms that make up the radish oil by the average molecular weight of the radish oil to obtain the relative fractions of carbon, hydrogen and oxygen:

$$C = \Sigma M(C)/ MOSRO =710.931/913.895 = 0.778;$$

$$H = \Sigma M(H)/ MOSRO =106.968/913.895 = 0.117;$$

$$O = \Sigma M(O)/ MOSRO =95.996/913.895 = 0.105.$$

Thus, the elemental composition of radish oil:

C = 0.778; H = 0.117; O = 0.105.

Further, we determined (Ukhanov, 2018) the elemental composition of the radish-mineral fuel in the ratios of plant and mineral components 25:75, 50:50, 75:25 and 90:10.

Viscosity (kinematic) and density were determined at 20°C experimentally using viscometer and areometer. The results of calculations and measurements are presented in Table 5.18.

Table 5.18

**Elemental composition, lower heat of combustion, density and viscosity of investigated fuels (Ukhanov, 2018)**

| Type of fuel | Elemental composition | | | Low calorific value, MJ $kg^{-1}$ | Density, kg $m^{-3}$ | Viscosity, $mm^2$ $s^{-1}$ |
|---|---|---|---|---|---|---|
| | C | H | O | | | |
| 100%DF | 0.870 | 0.126 | 0.004 | 42.40 | 830 | 4.2 |
| 100%OSRO | 0.778 | 0.117 | 0.105 | 37.37 | 922 | 78.4 |
| 25%OSRO+75%DF | 0.847 | 0.124 | 0.029 | 41.24 | 885 | 23.0 |
| 50%OSRO+50%DF | 0.824 | 0.121 | 0.055 | 39.89 | 897 | 41.5 |
| 75%OSRO+25%DF | 0.801 | 0.119 | 0.080 | 38.66 | 908 | 60.0 |
| 90%OSRO+10%DF | 0.787 | 0.118 | 0.095 | 37.89 | 914 | 71.0 |

Note: C, carbon; H, hydrogen; O, oxygen.

The results of the research show that red oil has a significantly higher density and viscosity compared to the corresponding indicators of commercial mineral DF, but when the share of mineral fuel in the blended fuel increases, the difference in values decreases significantly. The lower heat of combustion of red oil is equal to 37.37 MJ $kg^{-1}$, which is 11.9% lower than the corresponding index of commercial mineral DF. When the share of mineral fuel in DCT increases, the lower heat of combustion increases. So, for example, for blended fuel 25%OSRO+75%DF it is equal to 41.24 MJ $kg^{-1}$, which is lower than the corresponding indicator of mineral fuel by only 2.8%.

Table 5.19

**Comparative power, fuel-economic and environmental performance of diesel engine when operating on blended red-mineral fuel and mineral diesel fuel (Ukhanov, 2018)**

| Type of fuel | Diesel performance | | |
|---|---|---|---|
| | effective power, kW | specific effective fuel consumption, g $k^{-1}Wh^{-1}$ | smokiness, % |
| 100%DF | 56.1 | 252.4 | 45 |
| 25%OSRO+75%DF | 53.5 | 272.9 | 41 |
| 50%OSRO+50%DF | 53.0 | 279.3 | 39 |
| 75%OSRO+25%DF | 52.4 | 286.3 | 48 |
| 90%OSRO+10%DF | 52.0 | 292.3 | 51 |
| 90%OSRO+10%DF(US) | 53.2 | 283.8 | 50 |

OSRO – oilseed radish oil; DF – diesel fuel; DF(US) – diesel fuel treated with ultrasound

Comparative results of bench tests of diesel engine (Ukhanov, 2018) when operating on blended radish-mineral fuel in the ratio of components 25%OSRO+75%DF, 50%OSRO+50%DF, 75%OSRO+25%DF, 90%OSRO+10%DF and 90%OSRO+10%DF(US) show that with the increase in the content of radish oil in the blended fuel there is a slight decrease in the effective power and increase in the specific effective fuel consumption (Table 5.19). Thus, when operating on blended fuel with the ratio of mineral and vegetable components 90:10, the effective power of the diesel engine decreased from 56.1 kW to 52 kW (by 7.9 %), specific effective fuel consumption increased from 252.4 g/kW-h to 292.3 g/kW-h (by 15.8 %) in comparison with operation of the diesel engine on mineral fuel. The minimum exhaust gas smokiness is noted at operation on blended fuel 50%OSRO+50%DF and makes 39 %, which is 15,4 % less than at operation of diesel engine on mineral fuel.

Treatment of blended fuel with ultrasound allows to improve the performance of the diesel engine. So at work of a diesel engine on blended fuel 90%OSRO+10%DF(US) the effective power increases on 2,3 %, specific effective fuel consumption and smokiness decrease on 2,9 % and 2 % accordingly in comparison with work of a diesel engine on blended fuel 90%OSRO+10%DF not treated by ultrasound.

Commercial mineral DF and blended fuel in the ratio of components 25:75, 50:50, 75:25, 90:10, 90:10 (UZ 44 kHz) were taken as the investigated types of motor fuels. The studied fuels are characterized by the following parameters (according to the results of Ukhanov, (2018)):

Commodity DF: lower heat of combustion Hz = 42.4 MJ/kg; elemental composition C = 0.870, H = 0.126, O = 0.004; density ρ20 = 830 kg $m^{-3}$; viscosity υ20 = 4.2 $mm^2$ $s^{-1}$.

Red oil: Hz = 37.37 MJ/kg; C = 0.778, H = 0.117, O = 0.105; ρ20 = 922 kg $m^3$; υ20 = 78.4 $mm^2$ $s^{-1}$.

Blended redbed-mineral fuel:

– 25%OSRO + 75%DF: Hz = 41.24 MJ/kg; C = 0.847, H = 0.124, O = 0.029; ρ20 = 885 kg $m^3$; υ20 = 23.0 $mm^2$ $s^{-1}$.

– 50% OSRO + 50%DF: Hz = 39.89 MJ/kg; C = 0.824, H = 0.121, O = 0.055; ρ20 = 897 kg $m^3$; υ20 = 41.5 $mm^2$ $s^{-1}$.

– 75% OSRO + 25%DF: Hz = 38.665 MJ/kg; C = 0.801, H = 0.119, O = 0.080; ρ20 = 908 kg $m^3$; υ20 = 60.0 $mm^2$ $s^{-1}$;

– 90% OSRO + 10%DF: Hz = 37.89 MJ/kg; C = 0.787, H = 0.118, O = 0.095; ρ20 = 914 kg $m^3$; υ20 = 71.0 $mm^2$ $s^{-1}$.

As a result of comparative studies of the engine in bench conditions it is established (Ukhanov, 2018) that at operation of diesel engine D-243 at all investigated modes and blended red-oil-mineral fuel with different ratio of red-oil and mineral DF there is some deterioration of effective indicators of the diesel engine in comparison with operation on commercial mineral DF. Deterioration of indicators occurs as the content of cut oil in the blended fuel increases. So the decrease of effective power at work of the diesel engine in a nominal mode on a mixed fuel 90%OSRO + 10%DF has made 7,3 %, specific effective and hourly fuel consumption have increased accordingly on 6,3 % and 15,8 % in comparison with work of the diesel engine on mineral DF.

The analysis of ecological indicators of the diesel engine shows that when the share of red oil in the blended fuel increases up to 50 %, the exhaust gas smokiness decreases by 13.3 % (from 45 % to 39 %), and the content of carbon monoxide by 16 % (from 0.25 % to 0.21 %) in comparison with the operation of the diesel engine on mineral DF. With further increase in the proportion (more than 50 %) of red oil in the blended fuel, the environmental performance deteriorates.

The results of comparative diesel engine tests show that ultrasonic treatment of blended red oil-mineral fuel leads to improvement of diesel performance.

For example, the specific effective fuel consumption of a diesel engine running on a 90% OSRO + 10% DF (US) blended fuel increased by 12.4% compared to running the engine on mineral DF, while on untreated 90% OSRO + 10% DF blended fuel, the specific effective fuel consumption increased by 15.8% compared to running on mineral DF. The effective efficiency of a diesel engine running on a 90% OSRO + 10% DF (US) blended fuel is 1.8% higher than when running the engine on mineral DF.

Comparative studies of the tractor unit (MTZ-82 +PLN-Z-35) in operating conditions have shown that hectare fuel consumption increases as the percentage content of red oil in DST increases. So, when the diesel engine works on blended fuel 90%OSRO+10%DF its consumption is 25% more than when working on mineral DF. Operating speed, hourly productivity of the tractor unit and operating power of the diesel engine at work on blended fuel with mineral fuel are reduced insignificantly to 3,6 %; 3,8 % and 1,3 % respectively, in comparison with work on mineral fuel. The lowest exhaust gas smokiness is observed when the tractor is running on blended fuel 50%OSRO+50%DF and is equal to 31 %, which is 20,5 % less than when running on mineral DF. Ultrasonic treatment allowed to improve the studied operational indicators. Thus, when the diesel engine is running on blended fuel 90% OSRO + 10% DF (US) such indicators as operating speed (by 1.8 %), hourly productivity (by 2 %), operating power (by 0.6 %) increased and such indicators as hectare fuel consumption (by 3.4 %) and exhaust gas smoke (by 2.4 %) decreased in comparison with operation on non-treated blended fuel 90%OSRO + 10% DF.

As a result of comparative studies of the engine in bench conditions it is established that at work of diesel engine D-243 on all investigated modes and all kinds of blended red- mineral fuel some deterioration of effective indicators of the diesel engine in comparison with work on mineral DF is observed.

Deterioration of indicators occurs as the share of red oil in blended fuel increases. So the decrease of effective power at work of the diesel engine in a nominal mode on a mixed fuel 90%OSRO + 10%DF has made 7,3%, hourly and specific effective fuel consumption has increased accordingly on 6,3% and 15,8% in comparison with work of the diesel engine on mineral DF.

Analysis of the environmental performance of the diesel engine (Ukhanov, 2018) shows that when the share of cut oil in the blended fuel is increased to 50%, the exhaust gas smoke decreased by 13.3% (from 45% to 39%) and carbon monoxide content by 16% (from 0.25% to 0.21%) compared to diesel operation on mineral DF. With further increase in the proportion of red oil in the blended fuel, the environmental performance deteriorates.

The results of comparative engine studies (Ukhanov, 2018) of the diesel engine show that ultrasonic treatment of blended red-oil-mineral fuel leads to an improvement in diesel performance.

For example, the specific effective fuel consumption increased by 12.4 % when the diesel engine operated on blended fuel 90%OSRO+10%DF(US), whereas it increased by 15.8 % on untreated blended 90% OSRO+10% DF, compared to operation on mineral DF. The effective efficiency of diesel engine while running on blended fuel 90%OSRO+10%DF(US) is 1.8 % higher than that of diesel engine running on mineral DF.

The studies also showed that the environmental performance of a diesel engine improves when the content of radish oil in the fuel mixture is no more than 50 %: exhaust gas smoke is reduced by 21.4 %, and $CO_2$ concentration is reduced by 40 %. The greatest effect on environmental performance is achieved when the engine runs on a mixture of 25 % OSRO + 75 % DF. It was also found that the treatment of radish-mineral fuel with ultrasound has a positive effect on improving the environmental performance of the engine (Figures 5.4–5.7).

Based on the results obtained, the authors conclude that radish oil can be effectively used to prepare mixed diesel fuel. At the same time, the drop in tractor engine power does not exceed 7 %, and the increase in specific fuel consumption does not exceed 16 %. Ultrasonic treatment of mixed radish-diesel fuel improves these indicators by 2–4 %.

Thus, oil radish is not only a valuable fodder crop, but also a promising bioenergy crop, and by changing the parameters of oil radish cultivation

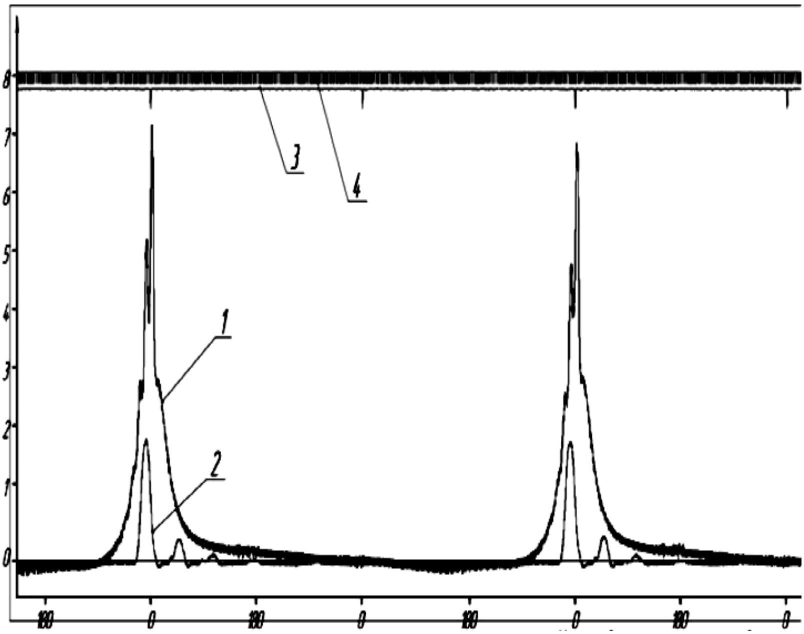


**Figure 5.4 – Indicator diagram of the D 243 engine in the rated power mode at 25 % OSRO + 75 % DF: 1 – gas pressure in the cylinder, 2 – fuel pressure in front of the injector, 3 – upper dead center indicator, 4 – flywheel teeth indicator) (Ukhanov, 2018)**

technology, it is possible to change the technological parameters of raw materials and regulate the “biofuel” productivity of a hectare of crops.

A comprehensive study of biodiesel from oil radish was conducted by Chammoun (2009). Two important properties for oilseed radish (Table 5.20) are iodine value and cold filter plugging point (CFPP).

The fatty acid profile identifies the carbon chain lengths and saturation of fatty acids in the triglycerides. It is important to note the high levels of 22:1, erucic acid, at 31.76% (Table 5.21).

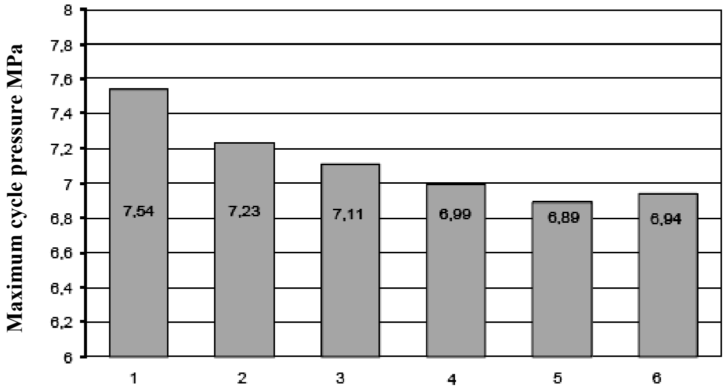



**Figure 5.5 – Maximum engine cycle pressure (MPa) of the D-243 in the rated power mode when operating on diesel mixed fuels: 1 – 100% VA; 2 – 25 % OSRO + 75 % DF; 3 – 50 % OSRO + 50 % DF; 4 – 75 % OSRO + 25 % DF; 5 – 90 % OSRO + 10 % DF; 6 – 90 % OSRO + 10 % DF (US) (Ukhanov, 2018)**

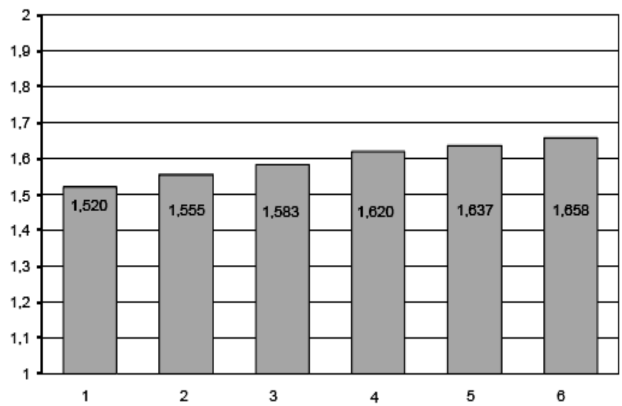



**Figure 5.6 – Air surplus ratio of the D–243 engine in the rated power mode when operating on diesel mixed fuels: 1 – 100% VA; 2 – 25 % OSRO + 75 % DF; 3 – 50 % OSRO + 50 % DF; 4 – 75 % OSRO + 25 % DF; 5 – 90 % OSRO + 10 % DF; 6 – 90 % OSRO + 10 % DF (US) (Ukhanov, 2018)**

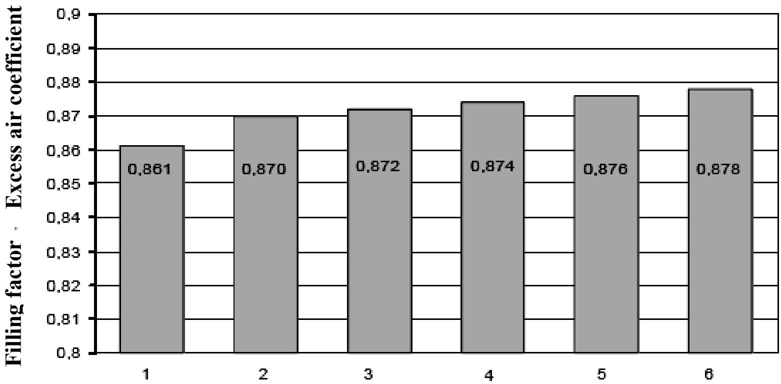



**Figure 5.7 – Filling factor of the D–243 engine in the rated power mode when operating on diesel mixed fuels: 1 – 100% VA; 2 – 25 % OSRO + 75 % DF; 3 – 50 % OSRO + 50 % DF; 4 – 75 % OSRO + 25 % DF; 5 – 90 % OSRO + 10 % DF; 6 – 90 % OSRO + 10 % DF (US) (Ukhanov, 2018)**

Table 5.20

**Oilseed Radish B100 Fuel Properties (Chammoun, 2009)**

| Parameter | Unit | Test Method | Result | Limit |
|---|---|---|---|---|
| Total Glycerol | % (m/m) | EN 14105 | 0.108 | < 0.24 |
| Free Glycerol | % (m/m) | EN 14105 | 0.000 | < 0.02 |
| Monoglyceride Content | % (m/m) | EN 14105 | 0.301 | < 0.80 |
| Diglyceride Content | % (m/m) | EN 14105 | 0.027 | < 0.20 |
| Triglyceride Content | % (m/m) | EN 14105 | 0.000 | < 0.20 |
| Acid Value | $mg_{KOH}/g$ | EN 14104 | 0.082 | < 0.50 |
| Sulfur Content | mg/kg | EN ISO 20846 | 0.790 | < 10.00 |
| Water Content | mg/kg | EN ISO 12937 | 68 | < 500 |
| Iodine Value | g/100g | EN 14111 | 97 | < 120 |
| Cold Filter Plugging Point (CFPP) | °C | ASTM 637199 | 6.0 | Report |

Rapeseed oil is considered non-edible oil because of the high levels of erucic acid. These levels were decreased by planting breeding and canola was developed. Canola is edible oil and is extensively in this capacity. If the erucic acid levels of oilseed radish were reduced, more uses of oilseed radish could develop while the presence of this oil lends it to unique industrial uses. It is also important to note that the remaining majority of the fatty acid profile is dominated by 18:1 (oleic acid) at 23.87%, 18:2 (linoleic acid) at 13.46%, and 18:3 (linolenic acid) at 10.34%.

Table 5.21

**Fatty Acid Profile of Oilseed Radish Oil (Chammoun, 2009)**

| Fatty Acid (n=3) | Percent (%) |
|---|---|
| 16:0 | 6.13 |
| 16:1 | 0.05 |
| 18:0 | 1.68 |
| 18:1 | 23.87 |
| 18:2 | 13.46 |
| 18:3 | 10.34 |
| 20:0 | 0.68 |
| 20:1 | 8.58 |
| 22:0 | 1.64 |
| 22:1 | 31.76 |
| 24:0 | 0.61 |
| 24:1 | 1.26 |
| Saturated | 10.74 |
| Monounsaturated | 65.51 |
| Polyunsaturated | 23.75 |

The coking indices for oilseed radish B100 and B20 both average 1.2 (Table 5.22). This is higher than the index of No. 2 diesel fuel, D2, of one. Usually biodiesel subjected to this engine stress test yield coking indices less than one. Results higher than one indicate this biodiesel may perform slightly less desirable than D2 and other biodiesel suggesting possible pre-mature wear on engine parts. To test for true differences between the biodiesel and D2, statistical analysis was done on the differences (delta) of the dirty and clean injectors. This difference is proportionate to the actual amount of coke deposited during the engine test. These deltas are also the numbers used to calculate the coking indices. The deltas are in six groups, D2A, D2B, B100A, B100B, B20A, and B20B. Two sample F tests were performed to determine if the variances of the six groups were statistically different. Since no differences were detected in the variances of the six groups, an Analysis of Variance (ANOVA) assuming equal variance was performed to detect statistical differences in the mean of the six groups. From the statistical analysis of the difference in areas of the coking on the injectors, there is no statistical difference in means of the six groups. Although the coking index for B20 and B100 oilseed radish biodiesel is higher than one, statistically there was no difference in the amount of coking on the injectors when biodiesel was tested over the baseline of D2. The coking index provides a quick assessment of the fuels performance, but the ANOVA gives actual differences between the groups. Statistical analysis is done on the deltas and not the coking indices because the coking indices do not allow for the variance of the D2 engine tests to be used in the analysis, since it is divided by itself to give a CI of one.

Table 5.22

**Coking Indices for Oilseed Radish Biodiesel (Chammoun, 2009)**

| Engine Test | B100 Coking Index | B20 Coking Index |
|---|---|---|
| 1 | 1.1 | 1.3 |
| 2 | 1.3 | 1.3 |
| 3 | 1.1 | 0.86 |
| Average | 1.2 | 1.2 |

The fuel consumption of D2 was observed to be less than that of B100 but not B20 (Table 5.23). A two sample F test was done on the six groups' recorded fuel consumptions, and a difference in variances was detected between the groups. The variances for B20A and B20B were the lowest at 308 and 933 respectively. The variances for B100A and B100B were 4008 and 25833; the variances for D2A and D2B were 33956 and 21683 respectively. The differences in variances were too large to continue the analysis with ANOVA, so the average fuel consumptions are displayed graphically (Figures 5.8–5.9).

The average emissions data for each fuel is presented graphically according to engine RPM when running at full throttle. If gas sensors were not operable, no data is presented for that fuel and the number (n) used in averaging is also reported. $CO_2$ emissions were recorded for one test each of D2 and B100, no B20 was recorded. A steady increase is CO2 is seen as loading on the engine increases. More CO2 output is the result of more fuel being combusted.

Table 5.23

**Fuel Consumption Indices for Oilseed Radish Biodiesel (Chammoun, 2009)**

| Engine Test | B100 Fuel Consumption Index | B20 Fuel Consumption Index |
|---|---|---|
| 1 | 1.0 | 1.0 |
| 2 | 1.2 | 1.0 |
| 3 | 1.3 | 1.0 |
| Average | 1.2 | 1.0 |

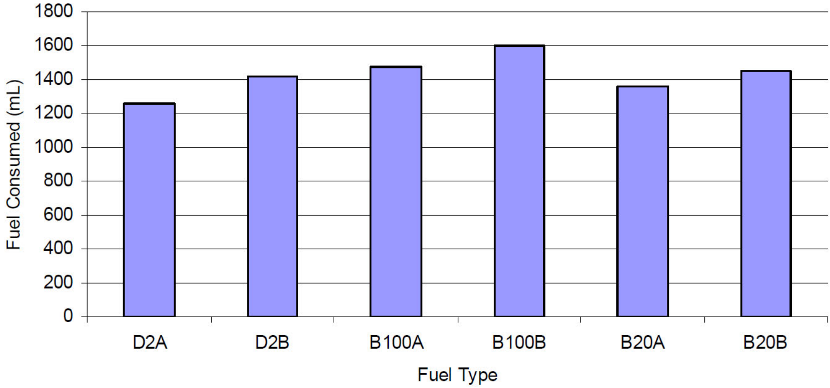



**Figure 5.8 – Average Fuel Consumption for Engines A and B using D2, B20, and B100B Oilseed Radish Biodiesel (Chammoun, 2009)**

A rapid jump in $CO_2$ emissions (Figure 5.10) is seen at the heavy engine loadings when more fuel is being consumed. As more fuel is consumed, more carbon is released thus the levels of CO increase. The increased in B100 CO emissions at heavier loadings is more than that of D2 or B20.

NOx emissions (Figure 5.10) show a marked increase of NOx in B100 over that of B20 and D2. This is what is typically reported in the literature, that biodiesel NOx emissions will increase over D2. But, this is the first time we have seen an increase in NOx in our engine testing. NO emissions and NOx emissions are essentially identical.

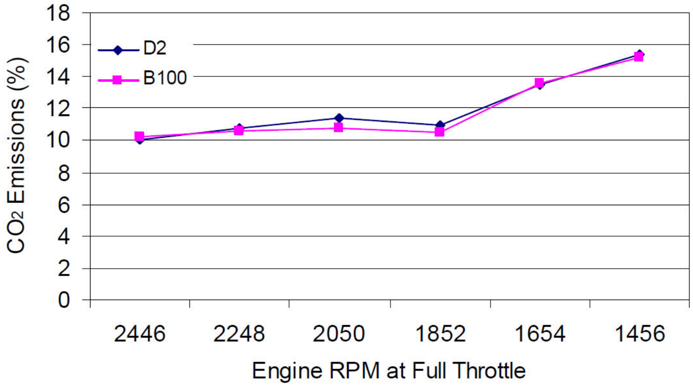



**Figure 5.9 – $CO_2$ Emissions of D2, B20, and B100 Oilseed Radish Biodiesel (n=3) (Chammoun, 2009)**

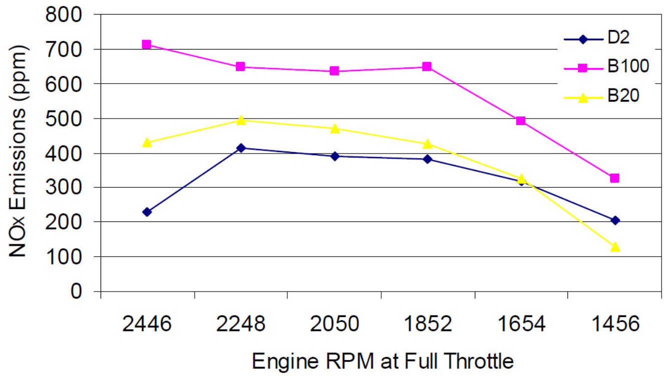



**Figure 5.10 – NOx Emissions of D2, B20, and B100 Oilseed Radish Biodiesel (n=3) (Chammoun, 2009)**

$C_xH_y$ emissions (Figure 5.11) are reported at one run each for D2 and B100, no data was recorded for B20. $C_xH_y$ emissions report hydrocarbon levels in fuel emissions. This would include any uncombusted fuel contained in the exhaust gases. Levels of hydrocarbons increase drastically at heavy loadings of the engine. This result is due to larger amounts of fuel consumption at the heavier loadings of the engine.

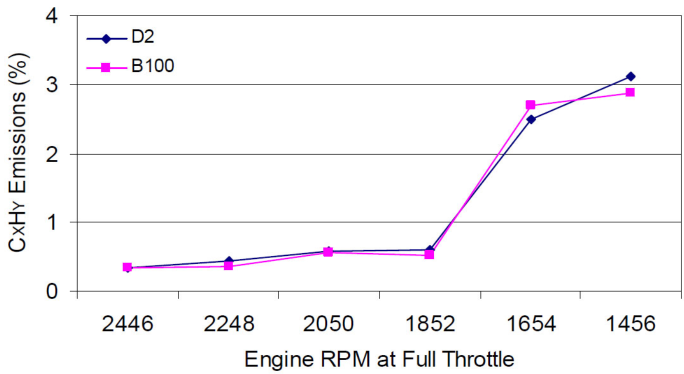



**Figure 5.11 $C_xH_y$ Emissions of D2 and B100 Oilseed Radish Biodiesel (n=1) (Chammoun, 2009)**

From the plots of iodine number versus CFPP, it does not appear that any trend can be observed in the plot. The R-squared values are too low to indicate a significant trend. Although, it is notable that when oilseed radish and crambe are removed from the data set and it is replotted, the linear, logarithmic, and $2^{nd}$ order polynomial trends improved based on the R-squared values. For these plots the oilseed radish data is from this study (Table 5.24, Figure 5.12), CFPP data is from Mittelbach and Remschmidt (2004), and iodine values are from Eckey (1954).

Table 5.24

**Iodine Numbers and CFPP Temperatures for Vegetable Oils and Their Fuels (Chammoun, 2009)**

| Oil/Fuel | Iodine Number | CFPP |
|---|---|---|
| Oilseed Radish | 97 | 6 |
| Soybean | 131.6 | -2 |
| Sunflower | 132.5 | -3 |
| Camellina | 140.5 | -1 |
| Tall Oil | 129.5 | -7 |
| Castor | 86 | -3 |
| Crambe | 100 | 8.5 |
| Olive | 84.5 | -6 |
| Poppy Seed | 137 | -1 |

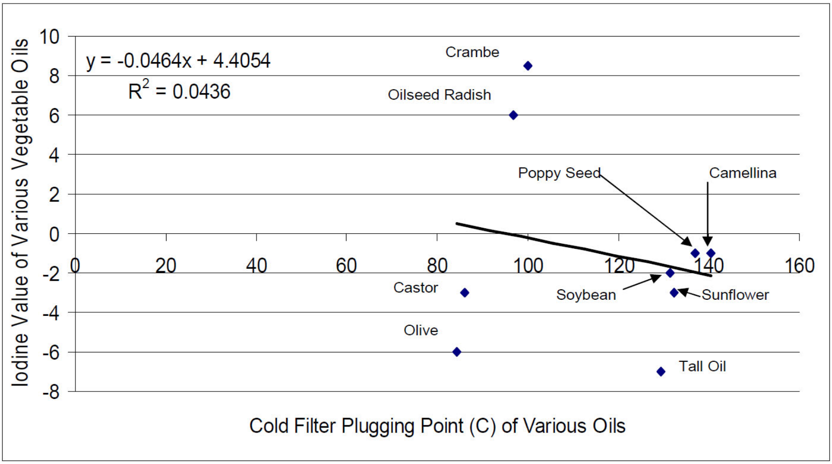



**Figure 5.12 – Linear Plot of Iodine Number vs. CFPP without Oilseed Radish and Crambe (Chammoun, 2009)**

From the crush results it can be concluded that oilseed radish can adequately be crushed using a screw type press in a one stage cold crush. With an average oil yield of 28.8%, the majority of the oil was extracted using only the cold crush. More oil could be obtained using either a second stage cold crush of the residual meal, or adding a solvent extraction step to the residual meal. It is believed more oil could be extracted from the cold crush if the process were optimized for oilseed radish seed size. Increasing the temperature of the seed would also yield more oil from the cold crush.

Fuel properties results indicate that it is possible to meet ASTM and EU standards for biodiesel using oilseed radish oil as a feedstock. The CFPP number for oilseed radish oil based biodiesel is high and would be a problem if a cold flow specification level was set. Currently CFPP is required to be reported and no threshold is set. If a threshold level is set, it is likely that oilseed radish cold flow would not ASTM or European standards. It is possible that future research on oilseed radish could lead to varieties that yield better CFPP numbers. Through plant breeding, more desirable cold flow properties could be bred into the crop for its use as a biodiesel feedstock. The high level of erucic acid seen in the fatty acid profile of oilseed radish is similar to that of rapeseed, a European biodiesel feedstock. Human toxicity of erucic acid will keep oilseed radish oil out of the food market, and thus improve its fit as a dedicated energy crop. Just as in cold flow properties, the levels of erucic acid could be decreased through plant breeding. Similar techniques were used to breed canola from rapeseed. Future work in this area could create additional markets for the crop.

Oilseed radish B100 and B20 shared a coking index of 1.2, although B100 would have been expected to have a higher coking potential than B20. Typically biodiesel produces lower coking indices than petroleum diesel; our results were contrary to this behavior. From the statistical analysis of coking deltas, there was not a statistical difference in the means of the deltas between any of the six groups; i.e. statistically each fuel performed on the same level. B100 or B20 from oilseed radish can be used in diesel engines without a statistical decrease in performance of the engine. Based on the fuel consumption indices, B20 performed the same as D2 and B100 performance was slightly less desirable at 1.2. But, since the variances within D2 and B100 were so high, further statistical analysis was determined to be unnecessary and coking indices are used to judge fuel consumption performance. Emissions data were not consistent enough for statistical analysis due to problems with gas sensors in the emissions testing equipment. For this reason the emissions data are presented as averages (if values were present) in graphs as a progression of loading and decreasing engine revolutions per minute (rpm). A relationship between iodine value and CFPP was determined to be less significant than predicted. When oilseed radish and crambe were removed from the plot, the r-squared value improved five fold. The leads us to believe that even though strong relationship was not established, oilseed radish and crambe lay outside the norm of other oils plotted. Both had high CFPP values, yet relatively low iodine values. The r-squared values lead us to believe that the relationship is more complex than originally believed. More research should be conducted to determine the relationship, if it exists, between cold flow and saturation of vegetable oils. One method would be to attempt the same analysis using pure triglycerides. If a relationship can be determined, a biodiesel from a particular vegetable oil can have a CFPP predicted before the oil is ever converted to biodiesel. This could serve as a rapid analysis for potential cold flow properties of a particular biodiesel feedstock.

There is need for future research into the agronomics of oilseed radish. Field trial should be done to quantify the agronomic benefits this crop has to offer in Georgia. Dr. Wilson Faircloth at the United States Department of Agriculture's National Peanut Research Laboratory in Dawson, Georgia is leading the effort to establish oilseed radish field trials. Dr. Faircloth reports excellent germination and crop growth throughout the cool season. Dr. Faircloth estimates harvest in adequate time to follow with a warm season crop. Although one season is not enough data to make any conclusions on the growth of the plant, it is a starting point in which future studies should be continued to assess the agronomic potential of oilseed radish. Since oilseed radish adds value to a cropping system as a cover crop, more research should be done to quantify these benefits and account for them along with the value of the oil for biodiesel feedstock. We believe that focusing attention on biofuel crops that have additional benefits to cropping systems in the form of improved soil fertility, pest protection, and soil health, is a route that should be pursued in future biofuel research. With the ever-changing dynamic of world fuel prices, additional value in a biofuel crop will increase the crop's ability to withstand large fluctuations in the fuel market. Added agronomic benefits also increase a producer's desire to grow a particular crop. Energy crops with agronomic benefits that can be used in crop rotations, lead to more sustainable farming practices and money savings to producers.

Oilseed radish oil was extracted, biodiesel produced and analyzed, and performance testing completed. The results verify that oilseed radish biodiesel meets ASTM and European standards, and performance testing concludes oilseed radish performs on the same level as petroleum diesel.

According to Chammoun (2009) to evaluate economic feasibility all costs and returns must be calculated. Costs and returns are calculated on a per acre basis using a yield of 1200 pounds of oilseed radish seed production per acre. The costs and returns calculated are not actual costs and returns, but hypothesized costs and returns based on available data. For actual costs and returns, experimental data should be acquired from growth studies. The costs and returns calculated here assume a low input situation, i.e. planting and harvesting the crop only, no other production costs considered. Hypothesized Costs for Oilseed Radish. Seed costs consisted of $66.93 per acre with an additional cost of $15.00 per acre for planting and $36.25 per acre for harvesting the seed. A minimum input system is used during production; therefore no additional inputs were calculated for crop production. It is assumed that oilseed radish can be planted into the previous crop's residue without any additional soil preparation. At a seed crushing cost of $50.00 per ton, oilseed radish would cost $30.00 per acre; yielding 346 pounds of oil (28.8%) and 854 pounds of meal (71.2%) per acre. At a refining and degumming cost of $0.025 per pound, it would costs $8.64 per acre to refine and degum the oil. With oil to biodiesel yield of 96% and 7.5 pounds of oil per gallon, production would be 42.5 gallons of oil per acre. With biodiesel production costs of $0.70 per gallon of oil, $30.97 per acre would be the production cost for biodiesel. Total hypothesized costs per acre sum to $187.78. These calculations assume no loss in processing oilseed radish into crude oil and biodiesel. Additional costs not included could be fertilizer required to grow the crop in Georgia, pesticides required to limit pest damage, and additional labor costs. Since hypothesized costs are simplified, actual costs may be greater than hypothesized costs (Table 5.25).

In the third case, to produce biodiesel, seeds purchased from Johnny's Select Seeds of Winslow, Maine were crushed to obtain crude oil. Oil yield was 28.8% by weight (Chammoun, 2009); the remainder was in meal.

The oil was then centrifuged and degummed. The degummed oil was then successfully converted into biodiesel by transesterification. Growers of oilseed radish in the Willamette Valley of Oregon report yields ranging from 1200 pounds/acre to over 2000 pounds/acre depending on management practices. More intensely managed crops produce more seed yield. A yield of 40% oil by weight, gives a range of 64 to 107 gallons of oil per acre (7.5 pounds per gallon). At the experimental yield of 28.8% oil, the range of oil per acre is 46 to 77 gallons. It is important to note that this oil yield will be in addition to any warm season crop that is grown in rotation with oilseed radish. In a biofuels rotation designed to maximize oil production per acre, a warm season oilseed crop could be grown, i.e. peanut or soybean and then oilseed radish grown in the cool season to supplement the amount of oil produced per acre per year. Methodology of Economic Analysis.

Table 5.25

**Amino Acid Profile of Oilseed Radish Meal (Chammoun, 2009)**

| Amino Acid | W/W% g per 100 g sample (average n=2) |
|---|---|
| Taurine | 0.03 |
| Hydroxyproline | 0.22 |
| Aspartic Acid | 2.13 |
| Threonine | 1.35 |
| Serine | 1.13 |
| Glutamic Acid | 5.43 |
| Proline | 1.99 |
| Lanthionine | 0.00 |
| Glycine | 1.78 |
| Alanine | 1.45 |
| Cysteine | 0.92 |
| Valine | 1.64 |
| Methionine | 0.62 |
| Isoleucine | 1.25 |
| Leucine | 2.23 |
| Tyrosine | 0.95 |
| Phenylalanine | 1.26 |
| Hydroxylysine | 0.04 |
| Ornithine | 0.02 |
| Lysine | 1.83 |
| Histidine | 1.00 |
| Arginine | 2.43 |
| Tryptophan | 0.39 |
| Total | 30.04 |

Hypothesized returns were calculated from crop and biodiesel byproducts, and from savings of insecticides that would not be applied (to subsequent crops) based on the nematode controlling capabilities of oilseed radish. A 92% reduction in nematode populations was observed in field studies, therefore it is assumed that no additional nematode control would be needed after a crop of oilseed radish was produced. There is currently no market for oilseed radish meal. A potential value for oilseed radish meal is calculated using the crop's crude protein value of 35%. Making the assumption that the price of soybean is composed solely of its protein content and that oilseed radish meal can be priced proportionately; a 48% protein soybean meal price of $222.27 per ton would give a hypothesized oilseed radish meal price of $162.07 per ton. At the yield of 1200 pounds per acre of oilseed radish, $69.24 per acre is the hypothesized value of the meal. With a five year average price of $3.27 for biodiesel, potential biodiesel returns would be $138.87 per acre. A five year average crude glycerin price of $0.07 per pound and a yield of 10.59% glycerin, glycerin value per acre would be $2.46. A hypothesized savings of $18.24 per acre and $15.20 per acre would be saved on insecticide (aldicarb) and insecticide application costs, respectively. An application rate of 6 pounds of aldicarb per acre was used for nematode control based on the recommendation of the University of Georgia Extension Plant Pathologist cotton budget for soil pathogen control. A total return of $244.00 per acre leaves the overall system with a hypothesized net return of $56.22 per acre. With a net biodiesel value of $107.90 per acre and an oil yield of 346 pounds per acre, an implied oil value of $0.31 per pound can be obtained. The implied value is the price that can be paid to the producer for crude oilseed radish oil so that a breakeven point can be achieved in biodiesel production. This value is not so important since there is currently no market for oilseed radish oil, but it is provided as a means to compare with other vegetable oil prices. Additional returns that were not included, but may add value to the system, could be weed suppression, soil aeration, soil compaction reduction, and nitrogen trapping. In an actual costing situation, these benefits would need to be assigned an economic value and that value assessed. These values are important, but detailed studies are needed to quantify them. Since these benefits are not included, hypothesized returns calculated may be lower than actual returns.

Sensitivity analyses were done on seed costs, biodiesel price, meal price, total costs, and total returns. It is believed that lower seed costs would be available to growers once markets for oilseed radish were established. By subtracting a total hypothesized cost per acre without seed of $120.86 from total hypothesized returns of $244.00, a minimum breakeven seed cost of $123.14 per acre, or $4.93 per pound of seed, would be needed to return adequate money to pay for all costs. A seed sensitivity graph is obtained from the break even seed cost and the hypothesized seed cost per acre (Table 5.26, Figure 5.13–5.15).

Fuel prices change on a daily basis. For this reason it is necessary to calculate a hypothesized break even price for biodiesel. A hypothesized break even price for biodiesel can be obtained by subtracting hypothesized returns without biodiesel ($105.14) from total hypothesized costs ($187.78) and dividing by biodiesel production per acre (42.5 gallons). The hypothesized break even price for biodiesel would be $1.94 per gallon. This means the biodiesel price could decrease below the $3.27 level (but above $1.94), and net hypothesized returns would remain positive.

Table 5.26

**Hypothesized Costs and Returns for Oilseed Radish at 1200 lbs/acre yield and Low Input Growing System (Chammoun, 2009)**

| **Hypothesized Costs** | | | | |
|---|---|---|---|---|
| **Activity/Product** | **Unit** | **Number of Units** | **Price per Unit ($)** | **Price per Acre ($)** |
| Seed | Pound | 50 | 133.85 | 66.93 |
| Planting | Acre | 1 | 15 | 15 |
| Harvest | Acre | 1 | 36.25 | 36.25 |
| Seed Crushing | Ton | 0.6 | 50 | 30 |
| Refining/Degumming | Pound | 346 | 0.025 | 8.64 |
| Biodiesel Production | Gallon | 42.5 | 0.7 | 30.97 |
| Total Hypothesized Costs | | | | 187.78 |
| Hypothesized Returns | | | | |
| Meal | Ton | 0.427 | 162.07 | 69.24 |
| Biodiesel | Gallon | 42.5 | 3.27 | 138.87 |
| Glycerin | Pound | 35.1 | 0.07 | 2.46 |
| Aldicarb | Pound | 6 | 3.04 | 18.24 |
| Aldicarb Application | Acre | 1 | 15.2 | 15.2 |
| Total Hypothesized Returns | | | | 244.00 |
| Total Hypothesized System Value | | | | 56.22 |

Soybean meal prices change on a daily basis, and it is assumed that the hypothesized meal price for oilseed radish could change regularly as well. Because of this possibility it is important to calculate a hypothesized break even price for oilseed radish meal. The hypothesized break even price for the meal is calculated by subtracting total hypothesized returns without the meal ($174.77) from total hypothesized costs ($187.78) and dividing it by the amount of oilseed radish meal per acre (0.4272 tons). The hypothesized break even meal price for oilseed radish is $30.45 per ton.

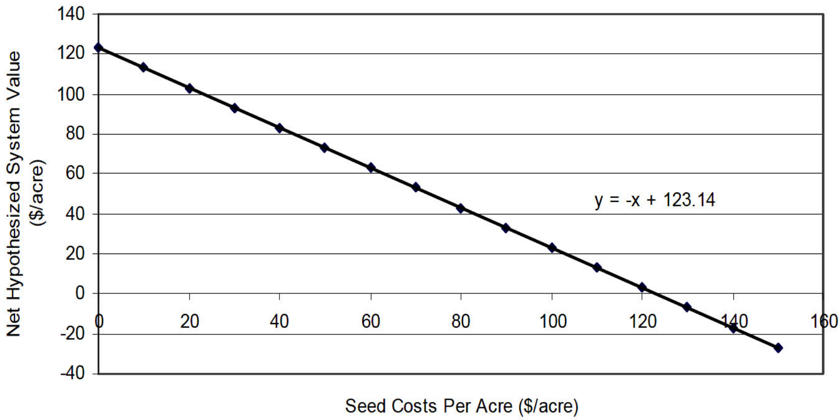



**Figure 5.13 – Sensitivity of Net Hypothesized System Value to Seed Costs Variation when Planting 25 lbs/acre (Chammoun, 2009)**

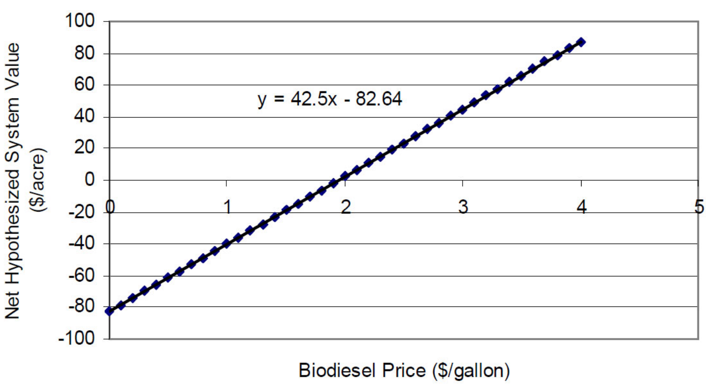



**Figure 5.14 – Sensitivity of Total Hypothesized System Value to Biodiesel Price Variation (Chammoun, 2009)**

Since many assumptions were made for this analysis it is possible that additional costs would be needed to produce the crop, or that additional returns could be generated from the crop. For this reason, a range of 20% was used to evaluate costs and returns if each were 20% higher or 20%

lower. If hypothesized costs were 20% higher, hypothesized returns would be adequate to cover hypothesized costs (Table 5.27). If hypothesized returns were 20% lower, hypothesized costs would not exceed the lowered hypothesized returns (Table 5.28). In fact, hypothesized costs would need to increase by approximately 30% to reach a breakeven point. In the same way, hypothesized returns would need to decrease by 23% to reach a breakeven point.

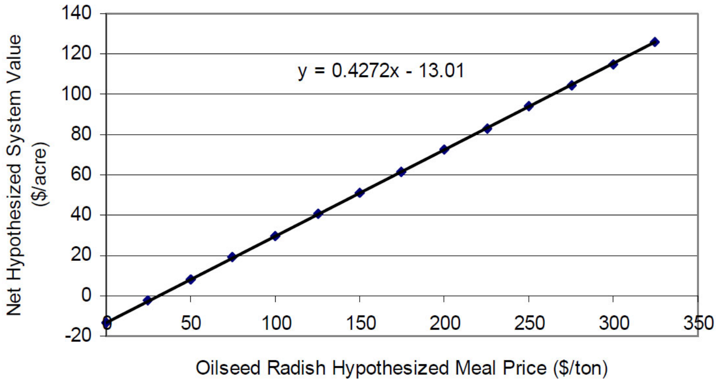



**Figure 5.15 – Sensitivity of Total Hypothesized System Value to Meal Price Variation (Chammoun, 2009)**

Table 5.27

**(+-) 20% Variation in Hypothesized Costs (Chammoun, 2009)**

| Variation (%) | Returns ($) | Costs ($) | Net ($) |
|---|---|---|---|
| -20 | 244.00 | 150.22 | 93.78 |
| -10 | 244.00 | 169.00 | 75.00 |
| 0 | 244.00 | 187.78 | 56.22 |
| 10 | 244.00 | 206.56 | 37.44 |
| 20 | 244.00 | 225.34 | 18.66 |

The author of this study (Chammoun, 2009) concluded that a hypothesized net return of $56.22 per acre, oilseed radish demonstrates potential to be a viable crop in Georgia, based on the assumptions made. An implied oilseed radish oil value based on biodiesel production of $0.31 per pound was hypothesized, and a hypothesized meal value was determined to be $69.24 per acre. A total hypothesized savings of $33.45 per acre could also be obtained when growing the next economic crop in rotation with oilseed radish if nematode populations were harmful.

Table 5.28

**(+-) 20% Variation in Hypothesized Returns (Chammoun, 2009)**

| Variation (%) | Returns ($) | Costs ($) | Net ($) |
|---|---|---|---|
| -20 | 195.20 | 187.78 | 7.42 |
| -10 | 219.60 | 187.78 | 31.82 |
| 0 | 244.00 | 187.78 | 56.22 |
| 10 | 268.41 | 187.78 | 80.63 |
| 20 | 292.81 | 187.78 | 105.03 |

A hypothesized break even cost for seed was determined to be $123.14 per acre which is above the hypothesized seed cost of $66.93 per acre. This difference in hypothesized value demonstrates that hypothesized seed costs could increase by approximately 84%, and a break even point still achieved. It is believed that seed costs would actually decrease after one year of growth. Seed could be saved by the producer to supplements seed for next year's crop. It is also believed that once more growers produce oilseed radish as a crop, the seed costs will decrease. The hypothesized break even biodiesel price was calculated to be $1.94 per gallon. The hypothesized break even biodiesel price is approximately 41% below the five year average price of $3.27 per gallon. The hypothesized breakeven price is useful to compare with current fuel prices to judge on the potential for oilseed radish biodiesel to be competitive in the biodiesel market. The hypothesized break even price for oilseed radish meal was calculated to be $30.45 per ton. This is below the hypothesized meal value of $162.07 per ton that is based on protein content. The large gap between the two prices demonstrates that the hypothesized meal price ($162.07 per ton) could decrease by 81% and hypothesized returns would still exceed costs.

Due to the limitations of the hypothesized calculations, a 20% variation in hypothesized costs and returns was calculated. If there was a 20% increase in hypothesized costs, and no increase in returns, hypothesized returns would still be greater than hypothesized costs. If there was a 20%

decrease in hypothesized returns, and no decrease in costs, hypothesized returns would still exceed hypothesized costs. This indicates improved potential for oilseed radish to succeed as a crop in Georgia. Even with a decrease in hypothesized system value, oilseed radish remains an attractive crop due to the un-valued benefits the crop can provide. Although values for soil aeration, soil compaction reduction, weed suppression, and nitrogen trapping may not be high, there is still added value in each of these benefits when oilseed radish is used in a crop rotation.

Oilseed radish meal also had high fat value, giving it a high energy value. The high fat value is due to the cold crush extraction method used, and no additional solvent extraction. The high fat content would increase the value of oilseed radish meal, and therefore increase the total hypothesized value of the system. More detailed studies are needed to allow for a more accurate method of evaluating the potential value of oilseed radish meal. Agronomic benefits should be evaluated with field studies done in Georgia to confirm nematode control levels, weed suppression levels, nitrogen trapping, soil aeration, and soil compaction reduction levels. Quantifying these additional benefits in Georgia soils, would allow for an economic evaluation to be done and a hypothesized value to be assigned, increasing the accuracy of the economic evaluation and adding value to the system.

Hypothesized costs and returns are limited by the assumptions used to calculate them. These assumptions were made in the absence of specific data for oilseed radish in Georgia. Oilseed radish is a new crop to Georgia; therefore no data was available for calculations. Assumptions were made based on data from other parts of the United States. Future studies are needed to gather data on oilseed radish in Georgia. The hypothesized system value shows potential for oilseed radish to succeed as a cover crop and biodiesel energy crop in Georgia. More importantly, crops such as oilseed radish should be considered in future crop rotations for their agronomic benefits and potential energy value. It is believed that energy crops with agronomic benefits will lead to more sustainable biofuel production, increased producer returns, and improved environmental health.

Oilseed radish as a feedstock for biodiesel was also highly evaluated in the study by Valle et al. (2009). The author concluded that oilseed radish – *Raphanus sativus* L. var. *oleiferus* Stokes – oil has been regarded as an interesting option to produce biodiesel, because the oil cannot be used for human consumption, the seeds have high oil content, and the cost of production is low. Furthermore, the plant has been used for green fertilization during the interval between harvests of other crops, due to its rapid development as well as its great ability to recycle nutrients. The content of free fatty acids in the crude oil is less than 0.5%, which makes it appropriate for basic catalyzed synthesis. However, basic catalyzed synthesis is very sensitive to the presence of water in the reaction environment. This study proposes the optimization of biodiesel synthesis using sodium ethoxide (sodium ethylate) as a catalyst, with the purpose of minimizing water formation during reaction, increase efficiency, and thus carry out transesterification in a single step. Ethanol was used instead of the methylic route, aiming at the production of an entirely renewable and environmentally preferable fuel. The experiments were proposed and carried out using a combination of fractional factorial design and Doehlert design, in order to allow an extensive study of the process variables with a minimum of experiments. Very intense levels of agitation and high temperatures proved to be inadequate to reach an effective reaction. At optimum conditions the ester content reached approximately 97.9%, which along with several other physical chemistry assays confirm the good quality of the product and that the synthesis of fodder radish crude oil can be performed in a single step efficiently.

The molar mass of fodder radish oil was calculated as 900.32 g $mol^{-1}$ based on its fatty acid composition shown in Figure 5.16 and Table 5.29 and on the acid number (0.7182 mgKOH $goil^{-1}$) determined by potenciometric titration.

Table shows some physical chemistry properties of the biodiesel from fodder radish oil obtained in our experiments that were performed according to the respective standard methods. All these analyses were carried out in triplicate, and the reported values are the average of the results. These results are in accordance with Brazilian legislation for biodiesel commercialization in the country and are strong evidence of the good quality of the product. The high ester content in the purified product (97.9%) shows that the reaction was very efficient, and it is important for the high performance of diesel engines.

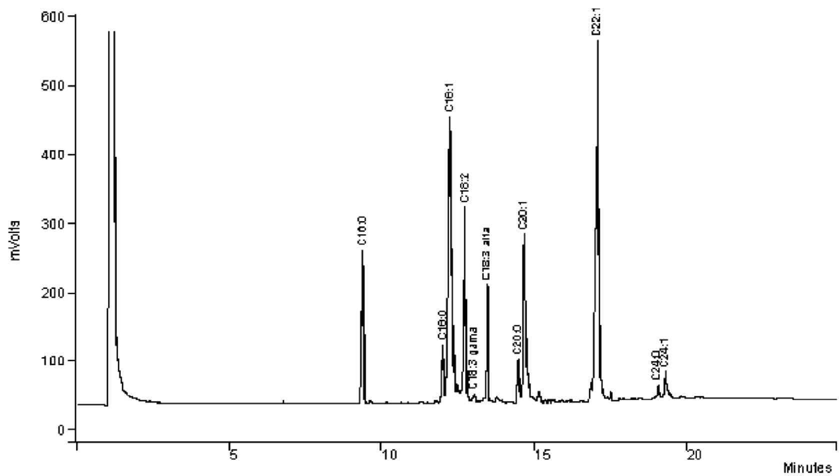



**Figure 5.16 – Chromatogram of Raphanus sativus L. var. Oleiferus Stokes oil fatty acids analyzed as methyl esters by gas chromatography using a capillary column (DB-Wax, 30 m x 0.25 mm i.d., 0.25 m, J&W Scientific). Detector (FID) and injector (split 1:100) at 260 °C. The FAMES were identified by comparing retention times to a standards mix (Supelco37) (Valle et al., 2009)**

Table 5.29

***Raphanus sativus* L. var. *oleiferus* Stokes Oil Fatty Acids (Valle et al., 2009)**

| Composition | | | |
|---|---|---|---|
| **fatty acid** | **CN:DB[a]** | **ret. time (min)** | **composition (% w/w)** |
| palmitic | 16:0 | 9.4 | 7.0 |
| stearic | 18:0 | 12.0 | 3.6 |
| oleic | 18:1 | 12.2 | 27.9 |
| linoleic | 18:2 | 12.7 | 7.6 |
| linolenic | 18:3 | 13.5 | 4.6 |
| arachidic | 20:0 | 14.5 | 2.2 |
| gadoleic | 20:1 | 14.7 | 11.2 |
| erucic | 22:1 | 17.1 | 33.3 |
| lignoceric | 24:0 | 19.1 | 0.6 |
| nervonic | 24:1 | 19.3 | 2.0 |

[ó] CN = carbon No.; DB = double bond

The specific gravity of 872.1 kg m$^{-3}$ and the kinematic viscosity of 5.511 mm$^2$ s$^{-1}$ guarantee that the fuel flows smoothly through the engine; it avoids excessive compression in the fuel injection pump and provides appropriate atomiza-tion in the combustion chamber, thus contributing to an efficient burning and to the low carbon deposits in the combustion area. This is confirmed by the result (0.03% w/w) of the carbon residue test (Table 5.30).

Table 5.30

**Phisical Chemistry Properties of Biodiesel from Fodder Radish Oil (Valle et al., 2009)**

| **properties aspect** | | **Brazilian specification** | **results LII[a]** | **methodology visual** |
|---|---|---|---|---|
| ester content | (% w/w) | minimum 96.5% | 97.9 | EN 14103 |
| specific gravity at 20 °C | (kg/m$^3$) | 850—900 | 872.1 | ASTM D 4052 |
| kinematic viscosity at 40 °C | (mm$^2$/s) | 3.0-6.0 | 5.511 | ASTM D 445 |
| flash point | (°C) | minimum 100[b] | 157.2 | ASTM D 93 |
| cold filter plugging point | (°C) | maximum 19 | 5 | ASTM D 6371 |
| carbon residue | (% w/w) | 0.05 | 0.03 | ASTM D 4530 |
| copper corrosion, 3 h at 50 °C | | maximum 1 | 1a | ASTM D 130 |
| Na + K | (mg/kg) | maximum 5 | 1.774[c] | ABNTNBR 15556 |
| Ca + Mg | (mg/kg) | maximum 5 | 1.509 | |
| P | (mg/kg) | maximum 10 | 0.446 | |
| acid number | (mg KOH/g) | maximum 0.5 | 0.21 | ASTM D 664 |
| iodine value | (g/100 g) | report | 96 | EN 14111 |

[a] Limpid and free from impurities.[b] If the flash is higher than 130 °C, it will not be necessary to determine the ethanol content.[c] This figure refers to Ca, because K was not determined.

The flash point was 157.2 °C. It indicates the temperature at which fuel vapors create a flammable mixture with atmospheric air, and it is important for safety in transport, storage and handling of fuel.

According to Brazilian laws, when flash point value is higher than 130 °C, the content of alcohol does not need to be determined. In this work, although the alcoholic content was not determined, the low values of Na (1.774 mg $kg^{-1}$) and Ca + Mg (1.509 mg $kg^{-1}$), as well as of the acid value (0.21 mg KOH $g^{-1}$) confirm the efficiency of the purification process, which aimed at removing the excess of alcohol, acid, and salts, as well as soaps and catalyst residues in the biodiesel. Copper corrosion test (1a) showed the low corrosiveness of the fuel, hence guaranteeing the integrity of the metallic parts of the engine. This result reveals the absence of sulfur components in the biodiesel.

Finally, the cold filter plugging point is a measure of the performance of fuel at low temperatures, and it is used as a handling indicator at low temperatures in the big flow tanks and in refinery and terminal pipelines. The result equal to 5 °C obtained for biodiesel from oilseed radish was far below the maximum limit (19 °C) established by Brazilian legislation.

The author of this study (Valle et al., 2009) concluded that the basis of the results achieved, it may be concluded that the use of sodium ethylate should be considered an interesting catalyst to the ethanolysis of fodder radish crude oil (Raphanus sativus L. var. oleiferus Stokes) because it reduces water production during the reaction and increases the efficiency of the transeseterification.

All the variables that affect the synthesis of biodiesel were studied: temperature, time, molar ratio, stirrer speed, and catalyst concentration. In the first stage of the work, the use of the 2(5–11) FFD showed that it is efficient in helping to select the most important variables, and allowed the reduction of the number of experiments at this stage. For the next stage, time, temperature, and catalyst concentration were selected and the other two factors were fixed at levels defined based on the results of the previous stage. The selected variables were studied in different levels in the Doehlert design of experiments and it showed to be very efficient (because it demanded few experiments) to find the optimum conditions (within the experimental domain studied) for the transesterification of fodder radish crude oil.

High temperatures, together with high concentrations of the catalyst and/or extended reaction times, tended to reduce the ester content in the products of the transesterification reaction. One of the reasons for this observation may be that these conditions can promote the formation of unwanted products (such as soaps), due to the occurrence of reactions that compete with the transesterification.

The optimum synthesis conditions obtained within the researched experimental domain were: reaction time = 70 min, reaction temperature = 30 °C, catalyst concentration = 1.3% w/w, with a molar ratio of ethanol/oil = 6:1, and a stirrer speed of 500 rpm. A very high stirring speed (over 500 rpm) was disadvantageous for the efficiency ofthe reaction. In these conditions, the ester content in biodiesel was 97.9% w/w. This ester content and all the other physical chemistry properties are in conformity with Brazilian regulation for commercial biodiesel and are strong evidence that the synthesis of biodie-sel from fodder radish crude oil can be carried out efficiently in a single step.

### 5.3. Oilseed radish as a raw material for biogas production

In 2009, the EU began to develop policies to ensure a 'sustainable energy union and long-term climate change policy'. As part of this project, the Renewable Energy Directive (RED) was created, which initially set a binding target of 20% of final energy consumption from renewable sources by 2020 (Kaletnik et al., 2020a,b; Tokarchuk et al., 2020). In Europe, as of 2022, 22% of the total primary energy supply comes from renewable sources. Of this share, more than half – 58% is biomass energy. In total, at the beginning of 2022, the European Union had 880 biomethane plants concentrated in 20 countries based on the use of biomass from various crops. The European Union plans to produce 35 billion cubic meters of biomethane by 2030 to replace 10% of conventional gas consumption. And by 2050, it wants to increase this share to 60 percent. The total potential for biomethane production in the world is 1.15 trillion cubic meters per year (EBA Statistical Report, 2023; Honcharuk et al., 2023 a, b). According to various estimates, 43–60% of this production potential is still generated from crop biomass (EBA Statistical Report, 2023).

At the same time, it is understood that achieving the noted potential and biogas production in terms of the use of biomass from specific crops requires a constant expansion of their range with a focus on the most adapted species with low resource capacity of their cultivation technologies for each country (Herrmann et al., 2016, 2016a; Komasilovs et al., 2021). Such monitoring is carried out on an ongoing basis, both from the point of view of in-depth study of traditional crops for biogas production in the total number of 25–30 species to the study of new crops, including wild species and even weeds (Zhang, 2021). Among these studied species, a group of cruciferous crops (spring and winter rape, white mustard, biomass waste from cabbage vegetable crops, and turnip) have proven to be effective candidates for biogas (biomethane) production both in the world and in Ukraine (Morozova, 2020; Jacob et al., 2021; Słomka & Oliveira, 2021; Gioulounta et al., 2023). At the same time, it is noted that a number of common crop species are not fully involved in the study of the efficiency and productivity of bomethane fermentation processes and the assessment of their possible and effective use in the system of alternative biofuel production (Molinuevo-Salces et al., 2013, 2013a; Zhang, 2021).

From this point of view, the classical oilseed radish (*Raphanus sativus* L. var. *oleiformis* Pers. (synonymously known as *Raphanus sativus* var. *oleifera* Metzg.)), a typical representative of the Cruciferous family with a wide range of adaptive properties and valuable biological traits, which is adapted to cultivation at different cultivation periods from early spring to late autumn with the possibility of full-species intermediate cultivation in crop rotations of different rotation (Tsytsiura, 2019, 2020a, 2021a,b, 2022a) is an attractive candidate for studying in the processes of biomethane production from its biomass. It is also noted that oilseed radish, from the point of view of forming a significant mass in a short period against the background of a wide range of adaptive properties and taking into account the appropriate levels of C/N ratio, can be considered as a potential candidate for the implementation of the goals of the green course and alternative bioenergy, since it combines the valuable properties of phytoremediation and phytomeliorant and the energy intensity of its biomass determined by the biomethanization process (Herrmann et al, 2014, 2016, 2016a; Hu et al., 2018; Qiao et al., 2018). At the same time, it should also be noted its importance as a green manure with intensive development of the root system, providing intensive soil drainage and replenishing the soil profile with a significant amount of organic matter against the background of the proven effect of anti-nematode activity and soil biofumigation (Rinnofner et al, 2008; Thiessen & EntzMartin, 2011; Jabnoun-Khiareddine et al., 2016; Hemayati et al., 2017; Jaskulska et al., 2017; Technical Note, 2020; Hansen et al., 2022). In addition, its positive effect on agrophysical properties and soil regimes, reduction of the level of total weeds under systematic cultivation as a predecessor and intermediate crop in crop rotations of different rotation intensities has been established (Lehrschb & Gallian, 2010; Chapagain et al., 2020; Tsytsiura, 2020b; Hudek et al., 2022). Its importance has also been proven from the point of view of using seed oil as a component of mixed biofuels (Ávila & Sodré, 2012; Chammoun et al., 2013; Faria et al., 2018; Tsytsiura, 2022b).

The noted agro-technological properties of oilseed radish can be attributed to a potential candidate for biomethane production, given that classical crops for biogas processing according to the basic principles of methane co-fermentation should be characterized by multifunctionality with the possibility of intermediate cultivation in crop rotation (MolinuevoSalcesi et al., 2014). In this regard, it is important to study such indicators as the net energy efficiency per hectare and biomass efficiency per hectare ($m^3$ $CH_4$ $ha^{-1}$) as important parameters for the application of intercrops as substrates in methane fermentation (Seppälä, 2013; Launay et al., 2022). Plant biomass, due to the high content of lignocellulosic substances, comprising mainly cellulose, hemicellulose, and lignin, requires pretreatment in order to improve susceptibility to biodegradation (Gioulounta et al., 2023). On the other hand, in recent years, interest in this crop has tended to grow, but its use as a component of bomethane production has focused on studying the efficiency of the cake after processing its seeds into oil for bomethane fermentation (Hu et al., 2018; Wendel et al., 2020; Junges et al., 2020). This significantly narrows its assessment in the areas of multi-purpose application directly in mobile biogas plants and stationary biofuel production directly within rural areas to ensure their bioenergy autonomy.

Taking into account the above-mentioned and the poorly studied biogas productivity of crude biomass of oil radish, the aim of the work was to investigate the biogas and methanogenic potential of oilseed radish (*Raphanus sativus* L. var. *oleiformis* Pers.) and to estimate the biogas efficiency of its biomass.

This research (Tsytsiura, 2023a) was carried out in 2020–2022 at Vinnytsia National Agrarian University (49°11′ N, 28°22′ E), during the potentially possible oilseed radish growing season of April-September (178 days). Height above sea level: 325 m. The area has a temperate continental climate. During the study period, the maximum and minimum temperatures were 18.3 °C in July and 15.8 °C in May, respectively. Mean annual relative humidity was 77% and mean annual precipitation was 480–596 mm.

The soil cover of the research field was represented by gray forest soils (Luvic Greyic Phaeozem soils) (IUSS Working Group, 2015) of medium loamy texture (according to the State Standard of Ukraine (SSU) ISO 11277:2005). According to the results of the agrochemical survey of the soil and the determination of basic indicators in accordance with national standards, it had the following agrochemical parameters (for the period of crop rotation) humus 2.02–3.20% (according to SSU 4289:2004), mobile forms of nitrogen 67–92 mg $kg^{-1}$ (according to SSU ISO 11261:2001), phosphorus 149–220 mg $kg^{-1}$ (according to SSU 4115-2002) and potassium 92–126 mg $kg^{-1}$ (according to SSU 4115-2002) with metabolic acidity of the soil solution ($pH_{KCl}$) 5.5–6.0 (according to SSU ISO 10390:2001).

The research was conducted using the variety 'Zhuravka', which is widespread in the region, using the method of pre-sowing design of its agrocenosis, which is used for the least costly variant of growing the crop in the research area with a sowing rate of 2.0 million seeds per ha using the conventional row method on an unfertilized background. The general scheme of the experiment with indexing options is presented in Table 5.31.

Table 5.31

**Factors of the experiment of biomethane productivity of oilseed radish leaf mass with preliminary silage fermentation (at four times replication (total combinatorics N = 48) (Tsytsiura, 2023a)**

| Factor of sowing time | Factor in the timing of leaf mass harvesting | Interaction of the factors |
|---|---|---|
| $A_1$ (budding stage, BBCH 50–53) | $B_1$ (I) | $A_1B_1$, $A_1B_2$, $A_1B_3$, $A_1B_4$ $A_2B_1$, $A_2B_2$, $A_2B_3$, $A_2B_4$, $A_3B_1$, $A_3B_2$, $A_3B_3$, $A_3B_4$ |
| $A_2$ (flowering stage, BBCH 64–67) | $B_2$ (II) | |
| $A_3$ (green pod stage, BBCH 73–75) | $B_3$ (III) | |
| | $B_4$ (IV) | |

The sowing dates were as follows: first (I) (second decade of April – early spring), second (II) (first decade of May – spring), third (III) (third decade of May – late spring), fourth (IV) (second decade of June – summer).

The hydrothermal regime of the period preceding sowing and the period of active vegetation was estimated by the hydrothermal coefficient (HTC) according to equation (5.8):

$$ГТК=\frac{\sum R}{0.1\times\sum t_{>10}}, \quad (5.8)$$

where is the sum of precipitation (ΣR) in mm for the period with temperatures above 10 °C, the sum of effective temperatures (Σt>10 ) for the same period, reduced by a factor of 10. Ranking of HTC values (Evarte-Bundere and Evarts-Bunders, 2012): HTC > 1.6 – excessive humidity, HTC 1.3–1.6 – humid conditions, HTC 1.0–1.3 – moderately dry conditions, HTC 0.7–1.0 – dry conditions, HTC 0.4–0.7 – very dry conditions.

The analysis of weather conditions and the level of their variability for the period 2013–2022 was carried out on the basis of the coefficient of significance of deviations ($C_{sd}$) of the elements of the agrometeorological regime of each of the studied years from the average long-term one in accordance with Equation 5.9:

$$C_{sd}=\frac{\left(X_i-X_{av}\right)}{S}, \quad (5.9)$$

where: $C_{sd}$ – coefficient of significance of deviations; current weather element; $X_{av}$ – indicator of the long-term average (at least ten-year period); S – standard deviation; i – year number. $C_{sd}$ level: 0 ÷ 1 – conditions are close to normal; 1 ÷ 2 – conditions differ significantly from the long-term average; > 2 – conditions are close to extreme.

According to the significance of deviations of the mean monthly value of the HTC from the average long-term data, the years of the study period by the value of Csd (Table 5.32, Figure 5.17) are classified as 2021 – dynamically variable with extremes of excessive moisture and extra-dry conditions, 2020 and 2022 – conditions close to typical for the long-term hydrothermal regime of the study area. The years of research in the order of increasing stress on the growth processes of oilseed radish plants from the standpoint of the dynamics of the amplitude of changes in average daily temperatures are as follows: 2022–2021–2020. The timing of leaf mass selection was set in accordance with the international scale of plant development BBSN (Growth stages of mono- and dicotyledonous plants) (Test Guidelines..., 2017), taking into account the possible achievable phenological stages of growth and flowering of oilseed radish plants, taking into account hydrothermal conditions in May-August, which are decisive in the levels of bioproductivity of this crop and are variably achievable at different sowing dates (Tsytsiura, 2019). Such phenostages of selection were the budding phase (BBCH 50–53), flowering (BBCH 64–67), and the beginning of the green pod (BBCH 73–75) (Figure 5.17–5.18).

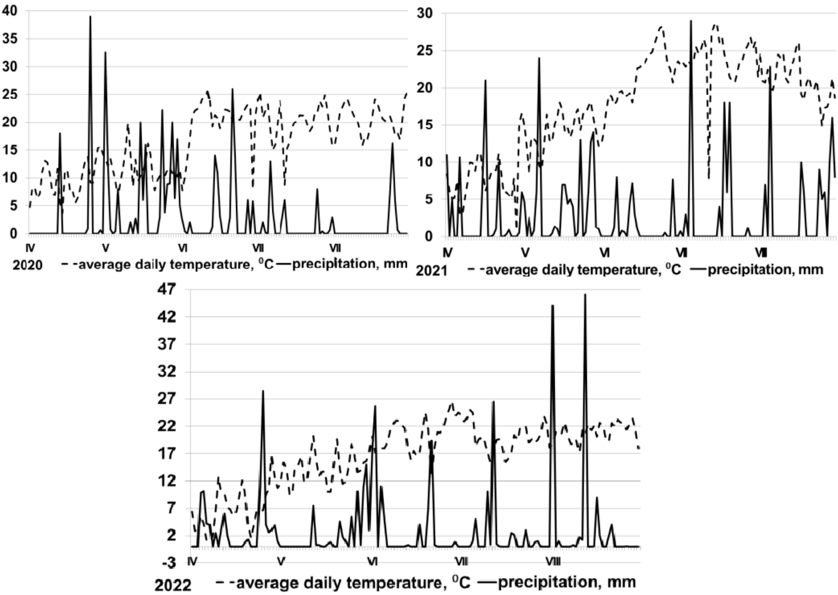



**Figure 5.17 – Average daily temperature (°C) and precipitation (mm) during the active vegetation period of oilseed radish of different sowing dates (May–August)**

In each phase of accounting, plants were cut at a height of 5 cm in the morning to minimize direct exposure to the sun on the tissues of cut plants and to maximize the preservation of turgor until shade drying and transported immediately to the laboratory for further analysis. Plant samples were collected from 1 $m^2$ plots at 4 randomly selected locations.

The characteristics of the plant mass were determined using a laboratory scale YP50002 (5 kg) with a discretion of 0.01 g. The resulting dried samples were re-weighed and ground using a Vilitek VLM-16 800 g 2200 mL electrostatic laboratory mill.

Table 5.32

**Estimation of GTC values during the active vegetation period of oilseed radish, 2020–2022 (Tsytsiura, 2023a)**

| Year of study | Months of the growing season | | | | | | | | On average for the period V–IX |
|---|---|---|---|---|---|---|---|---|---|
| | V | | VI | | VII | | VIII | | |
| | $X_i$ | $C_{sd}$ | $X_i$ | $C_{sd}$ | $X_i$ | $C_{sd}$ | $X_i$ | $C_{sd}$ | $C_{sd}$ |
| 2020 | 5.489 | 4.637 | 1.474 | -5.683 | 0.649 | -1.344 | 0.474 | -0.468 | -0.715 |
| 2021 | 0.530 | -0.322 | 1.077 | -6.080 | 1.589 | -0.404 | 1.513 | 0.571 | -1.559 |
| 2022 | 1.388 | 0.536 | 1.483 | -5.674 | 0.854 | -1.139 | 1.77 | 0.828 | -1.362 |
| $X_{av}$ (2013–2022) | 1.905 | | 1.385 | | 0.868 | | 0.725 | | – |
| S (2020–2022) | 2.236 | | 0.193 | | 0.435 | | 0.770 | | – |

The resulting biomass was divided into three types of analysis. The first involved its chemical analysis, the second – chemical analysis of oilseed radish silage obtained from its biomass at different sowing and harvesting dates, and the third – studying the dynamics of anaerobic digestion of oilseed radish silages (inoculum subtracted) depending on the options for its preparation by sowing and harvesting dates of the initial biomass.

Crop materials were chopped to a particle length of < 20–30 mm and preserved by ensiling. The laboratory silage process was carried out in 1.5-liter glass silos (J. WECK GmbH u. Co. KG, Wehr, Germany) immediately after grinding with pressing and full filling of the containers and subsequent hermetic sealing according to the methodology described in detail by Seale and Knap (2011), taking into account the methodology used in the studies of Herrmann et al. The closure system provided for the free release of gases generated during anaerobic fermentation. The temperature regime during 90 days of silage was constant at 25 °C ± 0.5. The silage was a single component without preservatives in quadruplicate for each experimental variant.

All laboratory chemical analyses applied to the obtained crushed samples of oilseed radish (moisture, ash, fat, protein and fibre content according to AOAC (2005) expressed on an absolutely dry weight basis) were carried out in quadruplicate in a specialized certified and accredited laboratory of Vinnytsia branch of the state institution 'Institute for Soil Protection of Ukraine' which is certified according to ISO 22000 international certification.

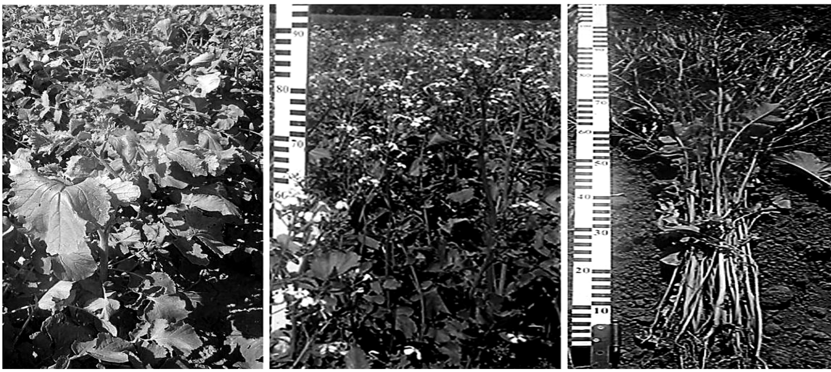


**Figure 5.18 – General development of Zhuravka oilseed radish plants (from left to right) at the budding stage (BBCH 50–53), flowering stage (BBCH 64–67), and beginning of green pod (BBCH 73–75), 2021 (Tsytsiura, 2023a)**

Crop materials of oilseed rape obtained from experimental plots of different sowing dates were wilted to a target DM content of 30–35% before the laboratory silage procedure (according to the recommendations of Herrmann et al. (2016)) before chopping and ensiling.

The obtained silage samples of different variants were subjected to low-temperature storage in a CRO/400/40 refrigerator (equipped with a temperature field control system) at 18 °C ± 0.5 after their removal from glass experimental silos according to the recommendation of Herrmann et al. (2016) before further processing for chemical composition analysis and biomethane production. The dry matter (DM) and organic dry matter (ODM) contents were measured by drying in an oven at 105 °C and then ashing the dried sample at 550 °C according to standard methods (AOAC, 2005). The dry matter content was adjusted to account for the loss of organic acids and alcohols during oven drying according to the recommendations of Herrmann et al. (2016).

The silage pH was determined using a high-precision combined pH electrode for continuous pH monitoring Sen Tix 41 (WTW, Weilheim, Germany, 2018 modification). Additional chemical components (lactic acid, volatile fatty acids, alcohols) were analyzed in cold silage extracts in the certified and accredited laboratory of the quality of crop products of Vinnitsa Oil Seeds Crushing Factory (private joint stock company). In particular, lactic acid was analyzed using a liquid chromatograph HPLC-1100 BIOEVOPEAK, taking into account the methodological recommendations of Xiao-song (2012) and Herrmann et al. (2016).

The analysis of volatile fatty acids (acetic, propionic, n-butyric, iso-butyric, n-valeric, iso-valeric, and n-caproic) and alcohols (ethanol, propanol, 1,2-propanediol, 2,3-butanediol) was performed using a Shimadzu GC-2014 gas chromatograph (modified with a capillary column and flame ionization detector) (Shimadzu Corporation, Japan).

Crude fat and crude fiber were determined according to the guidelines of Herrmann et al. (2014, 2016, 2016a) using standard laboratory methods (SSU (State standard of Ukraine) 8844:2019, SSU 8128:2015, SSU ISO 16472:2013, SSU ISO 7982:2015).

The elemental nitrogen content (Total Kjeldahl Nitrogen (TKN)) analysis of dry soil biomass was performed using the KjeLROC Kd-310 analyzer (ISO 17025) (in accordance with the State standard of Ukraine ISO 5983:2003, 2003 and SSU (State standard of Ukraine) 8108:2015). The content of total organic carbon (TOC) in the dry weight of plants after mechanical grinding was determined using a laboratory analyzer of total organic carbon of the TOC-LCPH series according to the standard protocol for low-temperature thermocatalytic oxidation of plant material.

Crude protein was calculated as the elemental nitrogen content multiplied by the standard conversion factor of 6.25, which is accepted with certain reservations for fresh and silage biomass of a whole group of crops of different species and families (Sáez-Plaza et al., 2013). The C/N ratio in silages was calculated as the ratio of elemental carbon to elemental nitrogen to assess the intensification of anaerobic digestion. Nitrogen-free extracts (NfE) were calculated as the difference between the content of 100% dry matter and the corresponding content of crude protein, crude fiber, crude fat and crude ash.

The assessment of the potential methane yield from laboratory silage samples with the determination of general parameters of its quality was investigated during anaerobic fermentation according to the general methodology proposed by Herrmann et al. (2016a) and Tang et al. (2020). For anaerobic fermentation, we used 1.0-liter glass vessels filled with 0.75 liters of inoculum and such an amount of plant material that the ratio of ODMS substrate to ODM inoculum was 0.5, taking into account the recommendations of Field et al. (1988) and Satyanarayana et al. (2008). Further actions to prepare the substrate for anaerobic digestion were carried out in accordance with the guidelines of Carvalho et al. (2011), which provided for bringing the final volume of the vessel to 700 mL with distilled water and normalizing the pH of the inoculum medium and silage substrate in the resulting mixture (based on the studies of Jayaraj et al. (2014) and Putra et al. (2023)) to 7.0–7.2 by corrective addition (if necessary, according to the preliminary control determination) of a 10M NaOH solution. As a control, a reactor containing only inoculum was used in order to discount that volume from the final volume of experimental variants. Anaerobic conditions in the laboratory reactors were created by flushing with nitrogen for 2/3 minutes immediately before closing the reactor.

Digestive enzyme obtained as a result of fermentation of pig manure for 14 days and obtained from the commercial enterprise 'Organic-D', which has a well-established biogas fermentation system of the European level of certification, was used as an inoculant. The resulting subtrate called 'Efluent' is certified in 2018 (Technical conditions of Ukraine 20.1-38731462-001:2018) and patented in Ukraine (Kaletnik et al., 2022 b; Lohosha et al., 2023). Based on the analysis in the Prime Lab Tech laboratory (according to the ISO 22000 international certification), this digestate had the following average chemical characteristics and standard deviation: pH 8.2 ± 0.3; DM 2.5 ± 0.7%; TDS 62.7 ± 3.3% of DM; N 2.9 ± 1.2 g $kg^{-1}$ ; $NH_4$–N 2.3 ± 0.7 g $kg^{-1}$; organic acids 1.7 ± 0.5 g $kg^{-1}$). The vessels were placed in a water bath with a constant temperature of 35 °C ± 0.5 with prolonged incubation for 60 days. Active shaking of the vessels was performed once a day at the same time. The biogas generated during the incubation period was collected in wet gas meters and recorded using a standard procedure for displacement of acidified saturated barrier solution with NaCl (VDI, 2006). The biogas volume was determined daily, corrected for the volume of biogas produced by the inoculum without substrate and normalized to standard conditions (dry gas, 0 °C, 1013 hPa). For this correction, the inoculum without substrate was subjected to the same anaerobic digestion procedure and used in the analysis of biogas production kinetics as a correction basis (according to Herrmann et al., 2016). Biogas composition for methane content was measured using a portable gas analyzer equipped with infrared sensors (HONEYWELL BW Flex, USA). The specific methane yield was calculated as the sum of methane produced during the test period per ODM of the silage sample in the corresponding experimental variant.

Kinetic analysis to determine the rate of biodegradation of silage samples during anaerobic digestion. For this purpose, standardized approaches were applied using the first-order differential equation (equation (3)) and the modified Gompertz equation (equation (5.10)) with fitting to the cumulative methane production curves (Lay et al, 1997 Mittweg et al., 2012) obtained during anaerobic digestion tests using the CurveExpert Professional v. 2.7.3 software package (Hyams Development) and Matlab R2016a software (TheMathWorks Inc., Natick, MA, USA).

$$y(t) = y_m\left(1 - e^{(-k_1 t)}\right), \tag{5.10}$$

where, y(t) is the cumulative specific methane yield at time $t$ ($L_N$ $kg^{-1}_{ODM}$), $y_m$ is the maximum specific methane yield at theoretically infinite digestion time ($L_N$ $kg^{-1}_{ODM}$), $t$ is the time (days) and $k$ is the first order decay constant ($day^{-1}$).

$$y(t) = y_m \exp\left[-\exp\left(\frac{Rm^e}{y_m}(\lambda - t) + 1\right)\right]$$ (after the transformation by logarithmization:

$$R_m = \frac{y(t)\left[In\left(In\frac{y(t)}{y_m}\right) - 1\right]}{e\left[\lambda - t\right]} \tag{5.11}$$

where, y(t) is the cumulative specific methane yield at time $t$ ($L_N$ $kg^{-1}_{ODM}$), $y_m$ is the maximum specific methane yield at theoretically infinite digestion time ($L_N$ $kg^{-1}_{ODM}$), $R_m$ is the maximum specific methane production rate ($L_N$ $kg^{-1}_{ODM}$ $day^{-1}$), $t$ is the time (days) and $\lambda$ is the lag phase (days), e = Euler's constant.

The lag period (λ) was defined as the period from the beginning of the anaerobic digestion test to the onset of methane emission, recorded in hours and subsequently converted to days with a conversion to a day length of 24 hours with the onset of gas emission recorded (based on the recommendations of Kim and Kim (2020)) using the MQ-4 methane gas sensor with the Arduino AVR Pic board.

The half-life ($t_{50}$) was determined based on the interpretation of the modified Gompertz equations as the time when 50% of the maximum specific methane yield is reached (days).

The degree of integrated connection of the biochemical composition of oilseed radish silage biomass with the main indicators of the kinetics of the productive process of biomethane production was estimated by the value of the coefficient of determination of the connection (Equation 5.12) and the use of the method of weighting the correlation graph in two interpretations according to Equations 5.13 and 5.14:

$$d_{yx} = r_i j^2 \times 100 \tag{5.12}$$

$$G = \sum_{|r_{ij}| \geq \alpha} |r_{ij}| \tag{5.13}$$

where $r_{ij}$ is the correlation coefficient between the i-th and j-th indicator. Only reliable correlation coefficients were used in the calculation.

$$G' = (\sum_{|r_{ij}| \geq \alpha} |r_{ij}|) / n \tag{5.14}$$

$n$ is the number of statistically significant correlation coefficients.

Statistical analysis of research results. It was conducted using Past 4.13 software (Øyvind Hammer, Norway) with the calculation of Pearson's correlation coefficients and multiple regression analysis according to the standard procedure (Wong, 2018). To compare the regression models, we used the coefficient of determination ($R^2$), adjusted coefficient of determination ($R^2_{adj}$), root mean square error (RMSE), and relative root mean square error (RRMSE).

The data obtained were analysed using analysis of variance (ANOVA) with determination of the share of influence of factors in the dispersion scheme. Tukey's HSD test in R (version R statistic i386 3.5.3) with multiple comparisons of the parameter means at the 99.9%, 99% and 95% family-wise confidence levels were used. In evaluating the obtained array of multiple values, standard indicators were used for analysing variable data (multi-year and genotypic components: $\bar{x}$ – average, SD – standard deviation, $C_v$ – coefficient of variation).

According to Herout et al. (2011) and Ahlberg and Nilsson (2015), the assessment of the potential of a particular crop for biogas production should necessarily include an assessment of both its bioproductivity in terms of the formation of an appropriate level of biomass yield and a general assessment according to the generally accepted chemical analysis structure. Taking into account these indicators allows us to draw a conclusion about the bioenergy potential of the species and the feasibility of its cultivation for biogas production. Evaluation of different sowing dates of oilseed radish, which are traditionally practiced in relation to this crop in the research area, proved a relatively high level of its bioproductivity both in early spring and summer with significant differences between the variants (Table 5.33).

Taking into account the findings on the comparable productivity of cruciferous crops for multiple uses (Maier et al., 2017; Sánchez et al., 2023), oilseed radish can be attributed to crops with high productive potential in terms of agrobiomass yield both in total weight and dry matter. There is also a steady tendency to decrease the level of biomass yield with a shift in the sowing dates of the crop.

Thus, the overall decrease in biomass yield with a sequential shift in sowing dates compared to the most productive first term was 12.41%, 39.97%, 51.23%, respectively, for the second to fourth applied terms. In terms of biomass yield in terms of dry matter, similar indicators amounted to 11.21%, 33.19% and 47.94%, respectively. The resulting factor of this trend is the change in hydrothermal conditions that develop during the period of active growth of vegetative mass for each sowing date with a certain nature of dependence in the form of regression equations (Table 5.34).

According to these equations, the efficiency of oilseed radish bioproductivity in terms of biomass yield depends on the ratio of precipitation and the increase in average daily temperatures. Taking into account the dimensionality of the regression analysis coefficients, the optimum for oilseed radish implies two main models of effective vegetation – sufficient moisture supply with a moderate rate of increase in average daily temperatures and a moderate moisture regime against the background of a stable temperature regime close to the optimum of physiological processes for cruciferous plants. Due to this nature, oilseed radish should be attributed to crops with optimal productivity, and therefore optimal regions of biogas application, belong to temperate regions with precipitation in May–July at the level of 220–250 mm and average daily temperature for the same period in the range of 16–18 ºC.

Table 5.33

**Oilseed radish biomass yield depending on the sowing date (average for 2020–2022), t ha$^{-1}$ ($\bar{x}$± SD) (Tsytsiura, 2023a)**

| Sowing date | Phenological stages | | | | | |
|---|---|---|---|---|---|---|
| | budding stage (BBCH 50–53) | | flowering stage (BBCH 64–67) | | green pod stage (BBCH 73–75) | |
| | 1 | 2 | 1 | 2 | 1 | 1 |
| I | 9.18 ± 1.15 | 0.93 ± 0.10 | 17.29 ± 2.62 | 2.18 ± 0.33 | 24.77 ± 3.18 | 3.67 ± 0.45 |
| II | 8.11 ± 1.42 | 0.80 ± 0.14 | 15.17 ± 2.08 | 1.85 ± 0.22 | 21.60 ± 2.78 | 3.37 ± 0.38 |
| III | 6.59 ± 1.40 | 0.71 ± 0.16 | 11.70 ± 2.73 | 1.62 ± 0.32 | 12.47 ± 3.50 | 2.20 ± 0.53 |
| IV | 5.87 ± 1.59 | 0.54 ±. 0.15 | 8.55 ± 3.11 | 1.28 ± 0.34 | 10.57 ± 2.90 | 1.71 ± 0.40 |
| Tukey‘s test ($R_{min}$ for $p_{adj}$ < 0.05) | 0.23–0.57 | 0.07–0.11 | 0.85–1.57 | 0.12–0.21 | 1.09–1.78 | 0.18–0.27 |

1 – in raw weight, t ha$^{-1}$; 2 – in dry matter (DM), t ha$^{-1}$.

Compensation for the negative effect of high average daily temperatures for oilseed radish according to the ratio of the coefficients of the regression equations ($X_1/X_2$ = 28–49) and taking into account the study (Ahmad, 2017) is possible in the case of intensive moisture at the level of 300–350 mm for the period May–July (with a decrease in the ratio between the coefficients of the regression equation to the level of $X_1/X_2$ = 20–28).

The chemical analysis of oilseed radish leaf mass also had significant differences with changes in the timing of sowing of oilseed radish (Table 5.35). The analysis of the presented indicators made it possible to estimate the rate of the so-called physiological aging of oilseed radish plants and the consideration of this factor in the suitability of its biomass for biogas production both in terms of changes in phenological phase s and changes in sowing dates. Comparing the phenological phase s of budding and green pod for the average sowing time, it was found that there was a steady tendency to decrease the content of crude protein by 37.52% and crude ash by 32.09%, increase the content of crude fat by 6.20%, crude fiber by 49.33%, with a relatively stable NfE (increase by 1.89%).

Table 5.34

**Regression dependences of oilseed radish biomass yield on hydrothermal conditions of the growing season in a single-model comparison of different sowing dates (in the total data set for 2020–2022 (N = 48)) (Tsytsiura, 2023a)**

| | |
|---|---|
| The yield of of leaf and stem mass (Y), t ha$^{-1}$ | Interphase period 'seedlings–flowering' |
| | $Y = 44.939 – 1.680X_1 + 0.059X_2$ ($R_{мн} = 0.753$. $R^2_{adj} = 0.517$. *p = 0.0007…0.004**) |
| | Interphase period 'seedling–green pod' |
| | $Y = 72.523 – 2.926X_1 + 0.0634X_2$ ($R_{мн} = 0.754$. $R^2_{adj} = 0.518$. *p = 0.001…0.004**) |
| Dry matter yield ($Y_1$), t ha$^{-1}$ | Interphase period 'seedlings–flowering' |
| | $Y_1 = 5.550 – 0.196X_1 + 0.004X_2$ ($R_{мн} = 0.730$. $R^2_{adj} = 0.477$. *p = 0.0001…0.048**) |
| | Interphase period 'seedling–green pod' |
| | $Y_1 = 10.077 – 0.388X_1 + 0.006X_2$ ($R_{мн} = 0.700$. $R^2_{adj} = 0.428$. *p = 0.0009…0.039**) |

Notes: 1. Climatic factors for the corresponding interphase periods of vegetation: $X_1$ – average daily air temperature, ºC; $X_2$ – precipitation, mm; 2. $R_{mn}$ – multiple correlation coefficient, $R^2_{adj}$ – adjusted coefficient of determination, * – actual p-level interval for the coefficients of the equation (at a minimum significance level of $p<0.05$).

At the same time, due to an increase in the content of total organic carbon by 7.96% against the background of an adequate decrease in the content of crude protein, the C/N ratio increased by 1.72 times. Certain regularities were also noted for the shift in sowing dates in the fourth-first comparison within the accounting phenological phases. For the budding phase, there was an increase in crude protein (and elemental nitrogen (TKN)) by 22.56%, organic carbon by 0.34%, and a decrease in the C/N ratio by 13.97%. For other side, the content of crude fat, crude fiber and crude ash increased by 37.60%, 24.68% and 34.22%, respectively, with a decrease in NfE by 23.48%. For the flowering phase, in the same variant of comparing the first and fourth terms, an increase in elemental nitrogen (TKN) by 6.76%, organic carbon by 1.64% with a decrease in the C/N ratio by 3.79% was noted.

Table 5.35

**Chemical composition of oilseed radish leaf mass by stages of growth and development depending on the sowing date and phenological phase of plants (average for 2020–2022) (Tsytsiura, 2023a)**

| Sowing date | Crude protein (CP) ($\%_{DM}$) | | | Crude fat (CF) ($\%_{DM}$) | | | Crude fibre (CFb) ($\%_{DM}$) | | | Crude ash (CA) ($\%_{DM}$) | | | NfE ($\%_{DM}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\bar{x}$ | SD* | $C_v$** | $\bar{x}$ | SD | $C_v$ | $\bar{x}$ | SD | $C_v$ | $\bar{x}$ | SD | $C_v$ | $\bar{x}$ | SD | $C_v$ |
| budding stage (BBCH 50–53) | | | | | | | | | | | | | | | |
| I | 13.12 | 2.40 | 18.29 | 2.58 | 0.53 | 20.54 | 17.22 | 3.83 | 22.24 | 13.12 | 1.12 | 8.54 | 53.96 | 4.76 | 8.82 |
| II | 14.13[c] | 2.17 | 15.36 | 2.22[c] | 0.46 | 20.73 | 25.14[a] | 5.11 | 20.33 | 13.24[d] | 1.89 | 14.27 | 45.40[b] | 4.69 | 10.33 |
| III | 19.27[a] | 2.61 | 13.54 | 2.14[c] | 0.52 | 24.30 | 21.52[b] | 4.72 | 21.93 | 18.07[a] | 3.90 | 21.58 | 39.00[a] | 5.44 | 13.95 |
| IV | 16.08[b] | 0.94 | 5.85 | 3.55[b] | 0.77 | 21.69 | 21.47[b] | 2.58 | 12.02 | 17.61[a] | 4.41 | 25.04 | 41.29[a] | 6.12 | 14.82 |
| flowering stage (BBCH 64–67) | | | | | | | | | | | | | | | |
| I | 13.89 | 1.11 | 7.99 | 3.04 | 0.27 | 8.88 | 21.77 | 4.62 | 21.22 | 12.58 | 2.55 | 20.27 | 48.72 | 4.56 | 9.36 |
| II | 13.63[d] | 0.62 | 4.55 | 2.73[c] | 0.32 | 11.72 | 26.91[a] | 5.89 | 21.89 | 12.53[d] | 1.42 | 11.33 | 44.20[c] | 4.71 | 10.66 |
| III | 17.48[a] | 1.65 | 9.44 | 2.75[c] | 0.52 | 18.91 | 23.12[c] | 5.34 | 23.10 | 14.17[b] | 2.83 | 19.97 | 42.48[b] | 7.38 | 17.37 |
| IV | 14.23[c] | 1.03 | 7.24 | 2.52[c] | 0.71 | 28.17 | 24.78[c] | 1.72 | 6.94 | 14.54[b] | 3.08 | 21.18 | 43.93[c] | 3.25 | 7.40 |
| green pod stage (BBCH 73–75) | | | | | | | | | | | | | | | |
| I | 8.08 | 1.12 | 13.86 | 3.14 | 0.98 | 31.21 | 32.31 | 6.73 | 20.83 | 8.39 | 0.68 | 8.10 | 48.08 | 8.18 | 17.01 |
| II | 8.92[c] | 1.66 | 18.61 | 3.61[c] | 0.78 | 21.61 | 32.34[d] | 7.13 | 22.05 | 9.04[c] | 1.99 | 22.01 | 46.09[c] | 2.35 | 5.10 |
| III | 11.44[b] | 2.85 | 24.91 | 2.04[b] | 0.20 | 9.80 | 31.88[c] | 5.27 | 16.53 | 11.27[a] | 1.32 | 11.71 | 43.37[b] | 3.29 | 7.59 |
| IV | 10.67[b] | 4.35 | 40.77 | 2.35[b] | 0.65 | 27.66 | 30.92[b] | 5.34 | 17.27 | 10.55[b] | 2.46 | 23.32 | 45.51[b] | 5.59 | 12.28 |

(End of Table 5.35)

| Sowing date | Total Kjeldahl Nitrogen (TKN) ($\%_{DM}$) | | | Total organic carbon (TOC) ($\%_{DM}$) | | | Ratio C/N | |
|---|---|---|---|---|---|---|---|---|
| | $\bar{x}$ | SD* | $R_V$*** | $\bar{x}$ | SD | $R_V$ | $\bar{x}$ | $R_V$ |
| budding stage (BBCH 50–53) | | | | | | | | |
| I | 2.10 | 0.38 | 1.72–2.48 | 37.47 | 2.08 | 35.39–39.55 | 17.84 | 15.95–20.60 |
| II | 2.26[c] | 0.35 | 1.91–2.61 | 38.12[b] | 2.29 | 35.83–40.41 | 16.87[b] | 15.48–20.33 |
| III | 3.08[a] | 0.42 | 2.67–3.50 | 37.63[c] | 2.82 | 34.81–40.45 | 12.22[a] | 11.56–13.04 |
| IV | 2.57[b] | 0.15 | 2.42–2.72 | 37.17[b] | 3.09 | 34.08–40.26 | 14.46[a] | 14.08–14.80 |
| flowering stage (BBCH 64–67) | | | | | | | | |
| I | 2.22 | 0.18 | 2.04–2.40 | 38.67 | 3.57 | 35.10–42.24 | 17.42 | 17.21–17.60 |
| II | 2.18[d] | 0.10 | 2.08–2.28 | 40.04[a] | 3.89 | 36.15–43.93 | 18.37[b] | 17.38–19.27 |
| III | 2.80[a] | 0.26 | 2.53–3.06 | 39.14[b] | 4.28 | 34.86–43.42 | 13.98[a] | 13.78–14.19 |
| IV | 2.28[c] | 0.16 | 2.11–2.44 | 39.37[b] | 4.63 | 34.74–44.00 | 17.27[c] | 16.46–18.03 |
| green pod stage (BBCH 73–75) | | | | | | | | |
| I | 1.29 | 0.18 | 1.11–1.47 | 41.03 | 3.89 | 37.14–44.92 | 31.81 | 30.55–33.45 |
| II | 1.43[c] | 0.27 | 1.16–1.69 | 40.92[c] | 4.17 | 36.75–45.09 | 28.62[a] | 26.69–31.68 |
| III | 1.83[b] | 0.46 | 1.37–2.29 | 40.38[b] | 4.55 | 35.83–44.93 | 22.07[a] | 19.63–26.15 |
| IV | 1.71[b] | 0.70 | 1.01–2.40 | 40.03[b] | 5.02 | 35.01–45.05 | 23.41[a] | 18.78–34.66 |

*SD – standard deviation; **$C_v$ – coefficient of variation, $R_V$ – range of values. Significance levels in comparison to the first (I) sowing term: a – 0.1%; b – 1%; c – 5%; d – no significant difference.

The crude fat content decreased by 17.11%, while the crude fiber and crude ash content increased by 13.83% and 15.88%, respectively, with a decrease in NfE by 9.83%. For the green pod phase, the elemental nitrogen and organic carbon content increased by 6.76% and 1.64%, respectively, with a decrease in the C/N ratio by 3.79%. Under the same conditions, crude fat, crude fiber, crude ash and NfE content decreased by 22.85%, 1.48%, 6.54% and 0.71%, respectively. According to the generalizations of Heiermann et al. (2009), Al Seadi et al. (2013), Tauš et al. (2020) and the presented data, the leaf mass of oilseed radish should be attributed to plants of potential candidates for biogas production through anaerobic digestion, with the optimum phenological phase use corresponding to the flowering phase of oilseed radish. It is for this phase that the necessary balance between the accumulation of fiber, nitrogenous compounds and nitrogen-free extractives has been established against the background of a variable hydrothermal regime. Such conclusions are also confirmed in the studies of Carvalho et al. (2011) and Molinuevo-Salces et al. (2013).

In the study by Herrmann et al. (2016), the period of possible biogas application of oilseed radish leaf mass covers the interval of BBCH 51–69 (end of budding and beginning of flowering phases). According to Belle et al. (2015), this phenological period also covers the beginning of fruit formation of oilseed radish plants, provided that it is combined with various wastes and manure.

The possibility of optimizing the suitability of plant biomass for anaerobic fermentation with methane production by preliminary silage has been investigated (Kreuger et al., 2011; López-Aguilar et al., 2023), which is most relevant for crops with a low C/N ratio and low dry organic matter content (Opurum, 2021; Hülsemann et al., 2023). Similar conclusions were confirmed in our research by applying the preliminary process of anaerobic silage fermentation to the options for harvesting oilseed radish leaf mass (Table 5.36).

It should be noted that previous studies (Ammann et al., 2009; Villalobos & Brummer, 2013; Zhou et al., 2021; Sánchez et al, 2023) emphasizes the value of oilseed radish as a silage crop during the phenological period of budding–flowering, but most researchers noted that due to the high moisture content of the mass and low values of the sugar minimum, its silage is difficult in a single-species composition, so preference should be given to combined silage of oilseed radish with cereals, cereal-legume mixtures and straw. Silage of oilseed radish in its pure form did not contribute to the long-term (traditional period of 4-6 months) preservation of the preserved mass before use. Depressurization of the silage mass at the beginning of its feeding led to a rapid deterioration in the quality of silage and a significant deterioration in its combinability. The appearance of a sharp unpleasant odor and rapid oxidation with blackening of the leaf-stem chopped mass was also characteristic of pure oilseed radish silage. It is for these reasons that the silage mass of oilseed radish can be considered as one of the components of biogas production, as emphasized in the studies of Carvalho et al. (2011), Molinuevo-Salces et al. (2013a) and Herrmann et al. (2016). The analysis of the chemical composition of silage mass of different terms and phases confirmed the technological reservations regarding the silageability of oilseed radish. Based on the level of alcohols and a number of acids (i-butyric, butyric, i-valeric, valeric and caproic acid) in the silage-fermented mass, a gradual increase in chemical stability and quality of silage was noted in the green pod phase. Thus, the concentration of these acids, when comparing the average time between the flowering and green pod phases, decreases by 2.58 times in favor of the latter phenological phase . A similar decrease with an index of 2.03 was observed for the concentration of alcohols in the silage mass. At the same time, the total acidity of the mass decreases by 0.4–0.6 pH units due to an adequate decrease in the content of a number of acids (lactic, acetic and propionic).

This dynamics is maintained with a similar character in the comparison of the first to the fourth sowing term). At the same time, the ratio of these acids (based on the studies of Rezende et al., 2015; Raboanatahiry et al., 2021; Chen et al., 2023; Wang et al., 2023) indicates a normal course of lactic acid fermentation and good preservation of leaf mass. Such features of biochemical changes are associated with the fact that in the fruiting phase (from the beginning of intensive green pod formation), the green mass of oilseed radish undergoes significant biochemical transformations, which opens up opportunities for independent silage of the leaf-stem mass of oilseed radish, due to a decrease in the buffering capacity of cell sap due to a decrease in the content of protein substances (Table 5.36) in plants during the approach and course of the generative phases of growth and development.

Table 5.36

**Dry matter, organic dry matter and chemical parameters of silage fermentation of oilseed radish depending on the sowing date and phenological stage of plants (average for 2020–2022) (Tsytsiura, 2023a)**

| Sowing date | Dry matter (DM), % | | Organic dry matter (ODM) ($\%_{DM}$) | | Crude protein (CP) ($\%_{DM}$) | | Crude fat (CF) ($\%_{DM}$) | | Crude fibre (CFb) ($\%_{DM}$) | | Crude ash (CA) ($\%_{DM}$) | | Ratio C/N | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\bar{x}$ | SD* | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD |
| budding stage (BBCH 50–53) | | | | | | | | | | | | | | |
| I | 11.51 | 1.17 | 73.62 | 0.21 | 11.92 | 0.23 | 2.89 | 0.15 | 18.27 | 0.21 | 14.63 | 0.14 | 18,42 | 0.18 |
| II | $10.84^{b}$ | 1.56 | $73.84^{d}$ | 0.33 | $12.87^{b}$ | 0.25 | $2.42^{c}$ | 0.17 | $26.27^{a}$ | 0.15 | $14.55^{d}$ | 0.18 | $17,96^{c}$ | 0.22 |
| III | $11.92^{c}$ | 1.41 | $74.41^{b}$ | 0.27 | $17.54^{a}$ | 0.65 | $2.51^{c}$ | 0.25 | $22.81^{a}$ | 0.17 | $19.52^{a}$ | 0.23 | $12,63^{a}$ | 0.36 |
| IV | $9.93^{b}$ | 1.74 | $72.92^{b}$ | 0.25 | $14.68^{a}$ | 0.36 | $3.79^{b}$ | 0.18 | $22.59^{a}$ | 0.09 | $18.69^{a}$ | 0.27 | $14,85^{a}$ | 0.29 |
| flowering stage (BBCH 64–67) | | | | | | | | | | | | | | |
| I | 13.82 | 1.08 | 82.57 | 0.18 | 12.55 | 0.15 | 3.41 | 0.17 | 22.93 | 0.18 | 13.74 | 0.28 | 18,39 | 0.23 |
| II | $14.55^{b}$ | 0.93 | $83.24^{c}$ | 0.15 | $12.37^{c}$ | 0.25 | $3.18^{c}$ | 0.19 | $28.17^{a}$ | 0.23 | $13.92^{c}$ | 0.13 | $19,57^{b}$ | 0.29 |
| III | $15.52^{a}$ | 2.29 | $83.78^{b}$ | 0.11 | $16.47^{a}$ | 0.42 | $3.22^{c}$ | 0.29 | $25.24^{a}$ | 0.27 | $15.79^{b}$ | 0.26 | $14,38^{a}$ | 0.31 |
| IV | $12.74^{b}$ | 1.57 | $81.77^{b}$ | 0.22 | $13.11^{b}$ | 0.64 | $2.97^{b}$ | 0.45 | $26.51^{a}$ | 0.10 | $15.84^{b}$ | 0.30 | $18,24^{a}$ | 0.38 |
| green pod stage (BBCH 73–75) | | | | | | | | | | | | | | |
| I | 16.85 | 2.14 | 88.27 | 0.12 | 7.04 | 0.69 | 3.61 | 0.42 | 33.27 | 0.22 | 10.17 | 0.12 | 34,37 | 0.38 |
| II | $17.73^{b}$ | 1.89 | $86.55^{b}$ | 0.15 | $7.49^{c}$ | 0.41 | $3.97^{c}$ | 0.26 | $34.11^{c}$ | 0.27 | $10.88^{c}$ | 0.30 | $32,64^{b}$ | 0.41 |
| III | $16.17^{c}$ | 1.74 | $85.17^{a}$ | 0.17 | $10.22^{a}$ | 0.25 | $2.58^{b}$ | 0.12 | $32.91^{c}$ | 0.17 | $12.51^{a}$ | 0.14 | $24,19^{a}$ | 0.27 |
| IV | $15.72^{b}$ | 2.27 | $84.38^{a}$ | 0.11 | $9.58^{a}$ | 0.55 | $2.92^{c}$ | 0.36 | $32.29^{c}$ | 0.19 | $12.08^{a}$ | 0.37 | $25,27^{a}$ | 0.30 |

(End of Table 5.36)

| Sowing date | Sum of i-butyric, butyric, i-valeric, valeric and caproic acid ($\%_{DM}$) | | Sum of ethanol, propanol, 1,2-butanediol, 2,3-propanediol ($\%_{DM}$) | | pH | | Lactic acid ($\%_{DM}$) | | Sum of acetic and propionic acid ($\%_{DM}$) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\bar{x}$ | SD* | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD |
| budding stage (BBCH 50–53) | | | | | | | | | | |
| I | 0.73 | 0.05 | 0.88 | 0.03 | 4.4 | 0.1 | 10.31 | 0.12 | 3.60 | 0.09 |
| II | $0.84^{c}$ | 0.09 | $0.98^{c}$ | 0.05 | $4.2^{c}$ | 0.1 | $11.12^{b}$ | 0.14 | $3.82^{c}$ | 0.07 |
| III | $0.62^{c}$ | 0.09 | $0.67^{b}$ | 0.08 | $4.1^{c}$ | 0.0 | $10.09^{c}$ | 0.18 | $2.74^{b}$ | 0.10 |
| IV | $0.96^{b}$ | 0.11 | $1.12^{a}$ | 0.07 | $4.2^{c}$ | 0.3 | $11.74^{b}$ | 0.11 | $3.55^{d}$ | 0.08 |
| flowering stage (BBCH 64–67) | | | | | | | | | | |
| I | 0.54 | 0.07 | 0.69 | 0.03 | 4.6 | 0.1 | 9.51 | 0.18 | 3.11 | 0.10 |
| II | $0.47^{d}$ | 0.05 | $0.58^{c}$ | 0.05 | $4.6^{d}$ | 0.0 | $8.07^{a}$ | 0.14 | $2.71^{b}$ | 0.12 |
| III | $0.41^{c}$ | 0.14 | $0.55^{b}$ | 0.07 | $4.8^{b}$ | 0.0 | $7.11^{a}$ | 0.16 | $2.24^{b}$ | 0.07 |
| IV | $0.72^{b}$ | 0.09 | $0.78^{c}$ | 0.09 | $4.5^{c}$ | 0.2 | $9.98^{c}$ | 0.09 | $2.92^{c}$ | 0.07 |
| green pod stage (BBCH 73–75) | | | | | | | | | | |
| I | 0.29 | 0.09 | 0.47 | 0.05 | 4.8 | 0.1 | 6.92 | 0.10 | 2.34 | 0.05 |
| II | $0.11^{a}$ | 0.08 | $0.32^{b}$ | 0.05 | $5.0^{b}$ | 0.2 | $6.45^{c}$ | 0.08 | $2.17^{c}$ | 0.05 |
| III | $0.38^{c}$ | 0.05 | $0.45^{d}$ | 0.07 | $4.8^{d}$ | 0.2 | $7.09^{c}$ | 0.07 | $2.07^{c}$ | 0.08 |
| IV | $0.44^{b}$ | 0.12 | $0.56^{c}$ | 0.11 | $4.7^{c}$ | 0.1 | $7.55^{c}$ | 0.12 | $2.39^{d}$ | 0.03 |

* SD – standard deviation; Significance levels in comparison to the first (I) sowing date: a – 0.1%; b – 1%; c – 5%; d – no significant difference.

Due to these biochemical transformations in the anaerobic process of silage fermentation, natural changes in the properties of all potential plant species occur (Herrmann et al. (2016): decrease in protein content against the background of an increase in crude fat, fiber and ash content. The well-known process of compaction of the chemical formula of the mass during anaerobic silage is also characteristic of cruciferous plant species (Borreani et al., 2018; Serhat et al., 2022). Due to the identified features, the stability of silage mass preservation of oilseed radish increased consistently from silage samples collected in the budding phase to the same samples collected in the green pod phase. The system of shifting the sowing dates from early spring (I) to summer (IV) changes this stability by creating conditions for active fermentation with the formation of a larger proportion of organic acids (an increase of 9.87% in the systems of the first to fourth sowing date) as a result of slow anaerobic decay processes. Such processes, according to studies (Satyanarayana et al., 2008; Kim and Kim, 2020; Tang et al., 2020; Opurum, 2021), indicate an increase in the share of associated gases in the total composition of biogas, in particular the share of hydrogen sulfide, nitrite derivatives, which ultimately leads to a predicted shortening of the lag period of the anaerobic fermentation process (López-Aguilar et al, 2023) and also leads to a general reduction in the duration of the period with biomethane release in the interval of the overall anaerobic fermentation process (Kalyuzhnyi et al., 2009; Kintl et al., 2022). That is, taking into account the chemical composition of oilseed radish silos of different studied variants, a more intensive biomethane production process with a greater variable component at the points of daily fixation should be expected with an increase in the proportion of fermentation associated gases for the mass harvested during the budding phase of later sowing dates. Gradually, with the physiological aging of oilseed radish plants, with the achievement of the flowering phase and the green pod phase, the process of biogas production will have a longer fixation interval, a more pronounced lag phase, with a decrease in the variability of the gas structure in the total volume of biogas productivity at the corresponding fixation dates. These features, taking into account the chemical composition of oilseed radish silage, are based on the conclusions of a number of studies (Mähnert et al., 2005; Abu-Dahrieh et al., 2011; Rodriguez et al., 2017; Darimani and Pant, 2020; Beausang et al., 2021; Jauhiainen, 2022; Szwarc et al., 2022).

Attention should also be paid to such a criterion as the C/N ratio, which, according to many researchers, determines the intensity of the biogas anaerobic fermentation process. The C/N ratios of cover crops generally vary from 9 to 40 (Zheng et al., 2004; Justes et al., 2012; Ma et al., 2018; Hansen et al. 2021; Yang et al., 2022). The optimal C/N ratio for anaerobic degradation depends on the substrate used, but a value between 20–30 is recommended (Kwietniewska et al., 2014; Wang et al., 2015). When a substrate has low C/N ratios, it is considered to contain relatively high ammonium concentrations, inhibiting microbial growth and anaerobic digestion (Cerón-Vivas et al. (2019); Choi et al., 2020). According to Choi et al. (2020), carbon to nitrogen (C/N ratio) has effects on methane production yield and it is a very important factor for stable operation. When the C/N ratio is too high, biogas yield does not show the optimum due to acidogenic bacteria rapidly consuming nitrogen compared to methanogenic bacteria. When the C/N ratio is too low, most microbes rapidly consume nitrogen for growth. Although this has a positive effect on methane production rate. However, the lack of carbon type causes that decrease in acid formation, nitrogen accumulates in the form of ammonium ions ($NH_4$) that increase the pH (Yen & Brune, 2007) which adversely affects biogas production. At the same time, despite the established optimal C/N interval (20–30), it is emphasized (Guarino et al., 2016) that this indicator has certain species-specific reservations based on the chemical characteristics of a particular agrobiomass and biogas production technology. Thus, according to the conclusions of the same Guarino et al. (2016), depending on the mode of biogas production, this interval had wider limits from 9 to 50, and in the studies of Dębowski et al. (2022) and Manyi-Loh et al. (2023), the optimal value of this ratio had a complex complementary nature of interaction and biomethane productivity of the anaerobic digestion substrate in the range from 10 to 30. Similar conclusions regarding the specificity of the formation of the C/N ratio were made in these studies. Thus, for fresh leaf mass (Table 5), the C/N ratio was in the range of 12.22-31.81 and had a steady upward trend as the plants aged phenologically. Thus, averaged over the sowing dates for the budding phase, this indicator was 15.35. At the flowering and green pod stages, it was at the level of 16.76 and 26.48, respectively. In view of the established optimal interval of 20-30 with a possible species deviation of 10-30 and the available value of the standard deviation in the assessment of annual variation, oilseed radish should be attributed to crops with a suitable capacitive ratio of biochemical composition, which determines a certain potential for biogas yield. Given that the first and second sowing dates have a long-term average of above 30 for the green pod phase, the optimal predicted period of use of crude plant biomass without preliminary silage fermentation is in the range of phenological development of the BBSN 64-70. On the other hand, this level of C/N ratio allowed us to note the value of oilseed radish leaf mass for green manure (green organic fertilizer), which is especially valuable, given a number of studies (Li et al., 2019; Liu et al., 2020; Hansen et al., 2021; Wang et al., 2021), when used in the budding-flowering phase of BBCH 50-64 with a C/N ratio of 12.22–18.37. The use of laboratory silage fermentation of oilseed radish leaf mass, which is consistent with the findings of Mähnert et al. (2005) and Abu-Dahrieh et al. (2011), ensured an increase in the C/N ratio for all experimental variants with an interval of 12.63–34.37, while maintaining the same trend within the phenological phases as in the variant before the use of silage fermentation. That is, the very process of silage of oilseed radish, which is confirmed by the peculiarities of the chemistry of silage fermentation of cruciferous crops (Kamalak et al., 2005; Raboanatahiry et al., 2021; Chen et al., 2023) allowed to optimize the variants by the C/N ratio.

The previous generalizations were confirmed in the assessment of the cumulative biogas and biomethane productivity of inoculated oilseed radish silage obtained from variants of different sowing dates at different phenological phases of harvesting (Figure 5.19).

The total volume of biogas production in the interval of harvesting phases (Figure 5.19 a) of leaf-stem mass was 2137–3643 mL with a maximum when using for preliminary silage fermentation the leaf-stem mass harvested in the flowering phase at the first sowing date of oilseed radish. The minimum value of this indicator was noted in the variant of the first sowing date for harvesting in the green pod phase. The level of variation of this indicator had different values within the combinatorics of the experimental variants. The maximum values of variation were determined for the fourth ($C_v$ 4.48–5.74%), and the minimum – for the first sowing dates ($C_v$ 1.69–3.88%). It should be noted that the achieved level of total biogas production is consistent with studies on biogas fermentation of oilseed radish agrobiomass in other studies. Thus, according to Belle et al. (2015), this figure was in the range of 2700–3100 mL. In the studies of Molinuevo-Salces et al. (2013, 2014, 2014a) it was at the level of 2200–3200 mL (in terms of the planted weight and silage options), and according to Carvalho et al. (2011) it reached the level of 3500–3700 mL. In comparison to other representatives of the cruciferous family (according to Herrmann et al. (2016), Maier et al. (2017), Liebetrau et al. (2021), Słomka & Oliveira (2021) and Lallement et al. (2023)) silage-fermented biomass of oilseed radish can be attributed to a crop with high biogas potential in comparison with such typical representatives as white mustard, spring and winter rape, and some wild species of cruciferous plants.

The difference in the variation of the indicator value can be explained by differences in the chemical composition of the leaf-stem mass determined for different phenological phases and harvesting dates, which led to differences in the chemical composition of the silage in the corresponding variant of the experiment. These are the reasons noted in the studies by Kalyuzhnyi et al. (2009), Borreani et al. (2018) and Lallement et al. (2023) from the point of view of the main factors that determine the potential biogas productivity of pretreated agrobiomass through silage fermentation.

The index of cumulative biomethane productivity (different variants of the experiment (Figure 4b) was determined in the range of 1215–1963 mL with a similar distribution within the variants of phenological development and sowing dates with an increase in the total variation to the average long-term value to the level of $C_v$ 4.08–8.40%. At the same time, for all terms of biomass harvesting, the fourth term had the highest level of variation with an index of 1.73 before the first sowing dates. This confirms the previously made conclusions about the peculiarities of the chemical composition of oilseed radish silages of summer sowing in terms of the presence of organic acids and the content of the main components, which, according to the study by Molinuevo-Salces et al. (2013), caused fluctuations in the share of methane in the total biogas composition and an increase in the share of other biogas components. These conclusions are confirmed by estimating the share of methane in the generated biogas volume (Figure 3c), where, in fact, for the fourth sowing term, an average minimum level of this indicator was noted at 54.34% (with $C_v$ 8.27–10.96%). The highest proportion of methane was noted on average for the phenological phase s of selection for the third sowing term with an average of 55.45% in the overall combination of experimental variants (at Cv 4.27–6.76%). At the same time, it should be noted, based on the interannual variability of indicators, a certain constancy of the intensity of anaerobic fermentation of oilseed radish silage, which is consistent with the findings of Rabemanolontsoa & Saka (2013), Bumbiere et al. (2022) on the relative species stability of agrobiomass of potential candidates for biogas production and the findings of McDonald et al. (1991), Herrmann et al. (2011, 2012) and Auxenfans et al (2017) on a certain leveling of the basic structure of chemical composition indicators under certain pretreatment procedures for biogas fermentation, including preliminary silage. According to Herrmann et al. (2016), for cruciferous crops, including fodder radish, the cumulative biomethane production for autumn sowing (intermediate cultivation) ranges (in terms of volume) from 900–1400 mL with a methane share of 53.9–57.3%. A number of other studies provide data on close values of the noted intervals (Carvalho et al., 2011, Suominen et al., 2012; Molinuevo-Salces et al., 2013, 2014, 2014a; AL-Huqail et al., 2022).

Based on the comparison of the results of the cumulative level of biogas productivity and the cumulative level of biomethane production, the specific methane yields of oilseed radish silages from different variants were in the range 201.03–319.66 $L_N\ kg^{-1}{}_{ODM}\ d^{-1}$ (group $C_v$ 12.95%) (the minimum was noted in the variant of the first sowing date for the green pod phase, and the maximum – in the variant of the first sowing date for the flowering phase). The average value of this indicator for the budding phase was 278.92 $L_N\ kg^{-1}{}_{ODM}\ d^{-1}$, for the flowering phase 292.45 $L_N\ kg^{-1}{}_{ODM}\ d^{-1}$, and for the green pod phase 237.54 $L_N\ kg^{-1}{}_{ODM}\ d^{-1}$.

Among the sowing dates, the maximum level of specific methane yields was achieved during the years of research at the fourth sowing date of 276.47 $L_N\ kg^{-1}{}_{ODM}\ d^{-1}$, and the minimum – at the third sowing date of 263.12 $L_N\ kg^{-1}{}_{ODM}\ d^{-1}$. This confirms the conclusions made earlier about the influence of changes in the biochemical composition of oilseed radish leaf biomass due to the shift in terms from early spring to summer on the features of the overall biogas productivity of the silage mass. In particular, this is an increased content of crude protein with a reduced content of crude fiber against the background of an increased content of nitrogen-free extractives, which forms optimal conditions for the intensity of biogas fermentation (Dandikas et al., 2014).

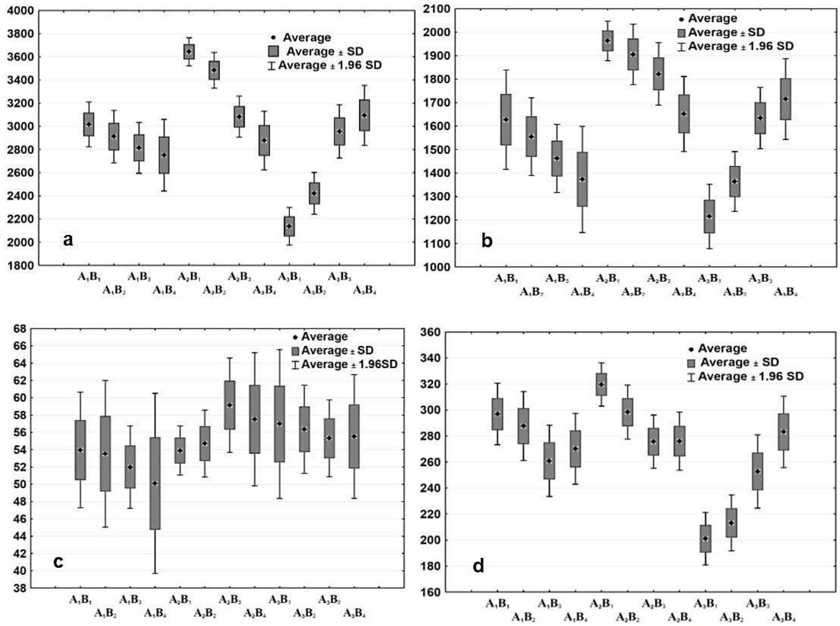



**Figure 5.19 – Statistical evaluation of biogas productivity of oilseed radish silages (inoculum subtracted) obtained from plant mass of different sowing and harvesting periods, 2020–2022 (a – cumulative biogas production during the experimental period (mL); b – cumulative biomethane production during the experimental period (mL); c – methane content (%); d – specific methane yields of oilseed radish silages from different variants (LN kg$^{-1}_{ODM}$ d$^{-1}$); $A_nB_n$ – indicates the combinatorics of options according to Table (Tsytsiura, 2023a)**

The determined interval for specific methane yields falls within the interval established in a number of studies specifically for the radish genus 170–350 $L_N$ kg$^{-1}_{ODM}$ d$^{-1}$ (Carvalho et al., 2011; Herrmann et al., 2016; Molinuevo-Salces et al., 2013, 2014, 2014a) although there is an upper limit of up to 350–380 $L_N$ kg$^{-1}_{ODM}$ d-1 and a lower limit of 120–150 $L_N$ kg$^{-1}_{ODM}$ d$^{-1}$ (Amon et al., 2007; Belle et al., 2015).

The cumulative curves of biomethane yield for different variants of research (Figure 5.20) confirm the conclusions made about the specifics of biomethane productivity from different variants of oilseed radish silage. At the same time, the maximum level of cumulative biomethane accumulation due to digestate inoculum was 656 mL over a period of 60 days of anaerobic fermentation, which corresponds to a sufficient level of cofermentation (Jankowska et al., 2017).

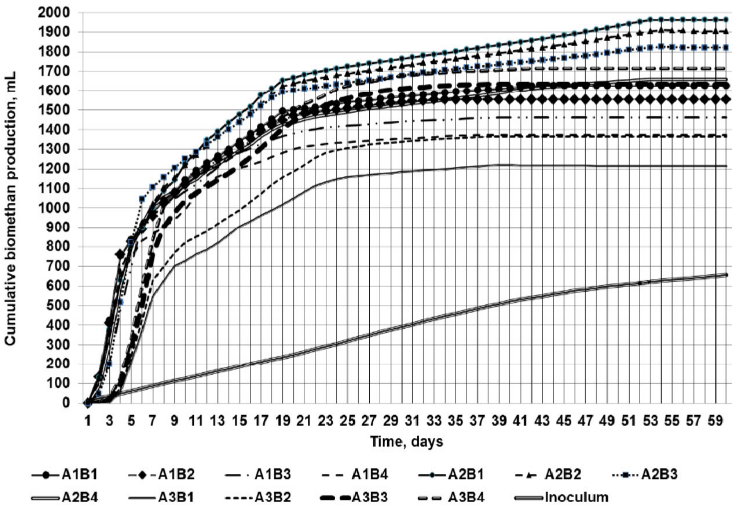



**Figure 5.20 – Cumulative biomethane production during the experimental period of oilseed rape silages (inoculum subtracted) obtained from plant mass of different sowing and harvesting dates, mL (average adjusted for biomethane productivity of inoculum and standardized dry gas indicators for 2020–2022 for the total number of observations for each variant) ($A_nB_n$ – indication of combinatorial variants according to Table 5.31) (Tsytsiura, 2023a)**

The cumulative curves correspond to the nature of the Gompertz growth curves (Lay et al., 1997), correlate adequately with the specified interval of values in the context of experimental variants, and have a complex shape mainly in the period of 3–21 days of fermentation. Taking into account the statement of Wang (2010), this character indicates the oscillatory nature of the formation of the indicator at the points of fixation with different ordinal placement of indicators with a pronounced downward structure of values in the dynamics. This is confirmed by the data in Figure 4b for each of the experimental variants when averaging each daily observation point.

The dynamics, while generally similar in the ordinal height of the graphs, has certain differences. Within the variant for the budding phase (indexing of variants $A_1$), an intensive increase in methane emission was noted on day 3–5 and dominated by oscillatory maxima in the interval of 7–10 days. The period of minimal biomethane activity was observed from day 23, and the complete cessation of the process from day 35–43. The most complicated idiogram of the graph for the budding phenological phase was observed for the variant of the fourth sowing date. A rather short lag period was established (average 1.32 ± 0.15 days).

For the phenological phase of flowering (indexing of variants $A_2$), a more smoothed character of the graph was noted. An intensive increase in methane emission was observed on day 3–4, followed by oscillatory maxima in the interval of 7–13 days. The period of minimal biomethane activity was observed from 26–29 days, and the complete cessation of the process from 39–42 days. The most complicated idiogram of the graph for the flowering phenological phase was noted for the variant of the first and fourth sowing dates of oilseed radish. The duration of the lag period increased and averaged 1.49 ± 0.13 days.

For the phenological phase of the green pod (indexing of variants A3), a complex oscillatory nature of the graph (three peak values) was noted. There was an intensive increase in methane emission on day 5–7 followed by oscillatory maxima in the interval of 13–19 days depending on the sowing date (indexing of variants $B_1$–$B_4$). The period of minimal biomethane activity was observed from 22–25 days, and the complete cessation of the process from 55–58 days. The most complicated idiogram of the graph for the flowering phenological phase was observed for the variant of the first and fourth sowing dates of oilseed radish. The duration of the lag period was maximum for this phenological phase for all sowing dates and averaged 2.09 ± 0.65 days with a maximum for the first sowing date.

The mathematical expression of the curves for the research variants (Figure 5.21a) in terms of cumulative biomethane productivity corresponds to the classical Gompertz functional dependence for the cumulative nature of growth, described by classical equation 5.8–5.9. This is confirmed by the results of approximating the actual curve points to the model functions with the estimation of the correlation and prognostic components (RMSE and RRMSE) (Table 5.37). This mathematical relation is fully consistent with the mathematical models of biogas production from both raw plant material of bioenergy crops and subjected to various preliminary procedures of preparation for the final biofermentation process and is reflected in a number of publications (Parker et al, 2005; Carvalho et al., 2011; Triolo et al., 2011; Podkówka, 2012; Thomsen et al., 2014; Batstone et al., 2015; Herrmann et al., 2016; Einarsson et al., 2017; Pabón-Pereira et al., 2020; von Cossel et al., 2021; Tasnim et al., 2022; Fajobi et al., 2023).

At the same time, a number of features were noted that distinguish oilseed radish as a potential candidate for biogas production. In particular, the value of the coefficient $k_1$ (the first order decay constant ($day^{-1}$)) in the equation of dependence on the anaerobic fermentation time (Table 6) determined for fodder radish in the studies of Herrmann et al. (2016) was in the range of 0.190–0.273, although among cruciferous crops in his studies, the value of this indicator was the lower limit of 0.144. In Słomka & Oliveira's (2021) research for white mustard, based on the analysis of the presented curves, this coefficient had a lower limit of 0.090–0.100. It is also reported (Ahlberg & Nilsson, 2015) that the nature of cumulative curves of biogas production can have a complex oscillatory character due to the specific biochemical composition of the biomass taken for fermentation, which can increase the value of this coefficient k at the starting sections of the curve and reduce its value for the overall analysis of the graph on the general abscissa of the graph. The same conclusions regarding the wide-interval value of the $k_1$ coefficient were noted in the studies of Herout et al. (2011) and Maier et al. (2017) At the same time, Fajobi et al. (2023) and Pabón-Pereira et al. (2020) noted that greater intensity of ordinal growth of the cumulative biogas production curve is characteristic of biomass with a lower dry matter content, rich in proteins and nitrogen-free extractives. This is confirmed by the results presented in the case of the budding phase, especially of the fourth sowing term, where a similar character of the biochemical composition of the plant mass is noted (Tables 5.36, 5.37) with a value of $k_1$ in the range of 0.122–0.134.

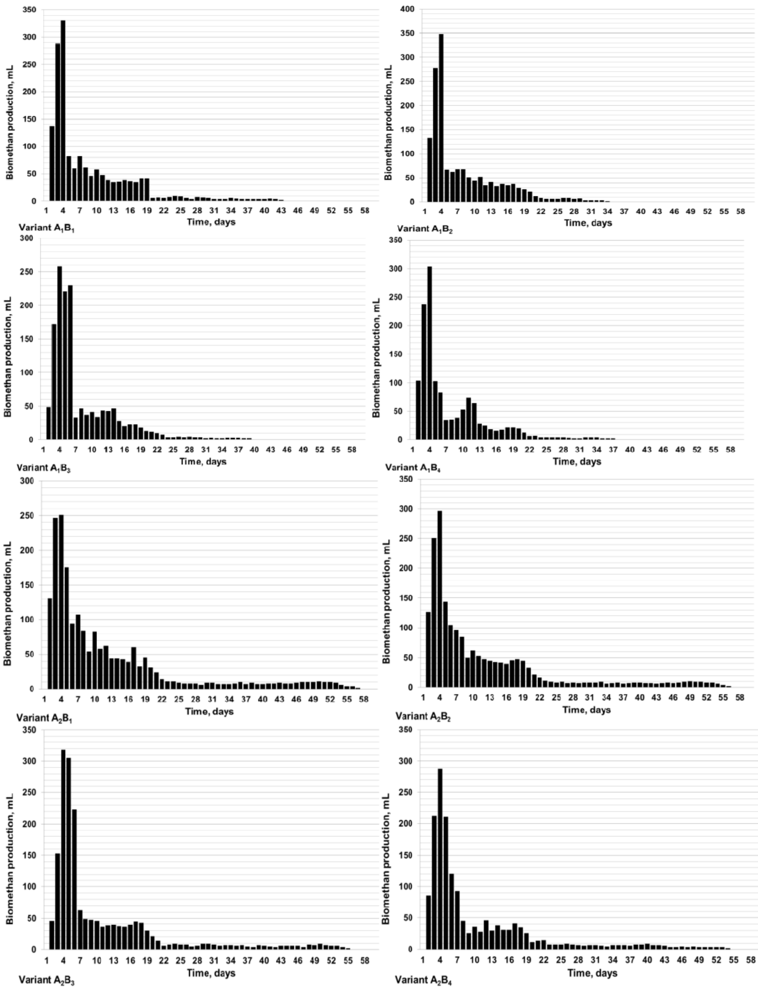
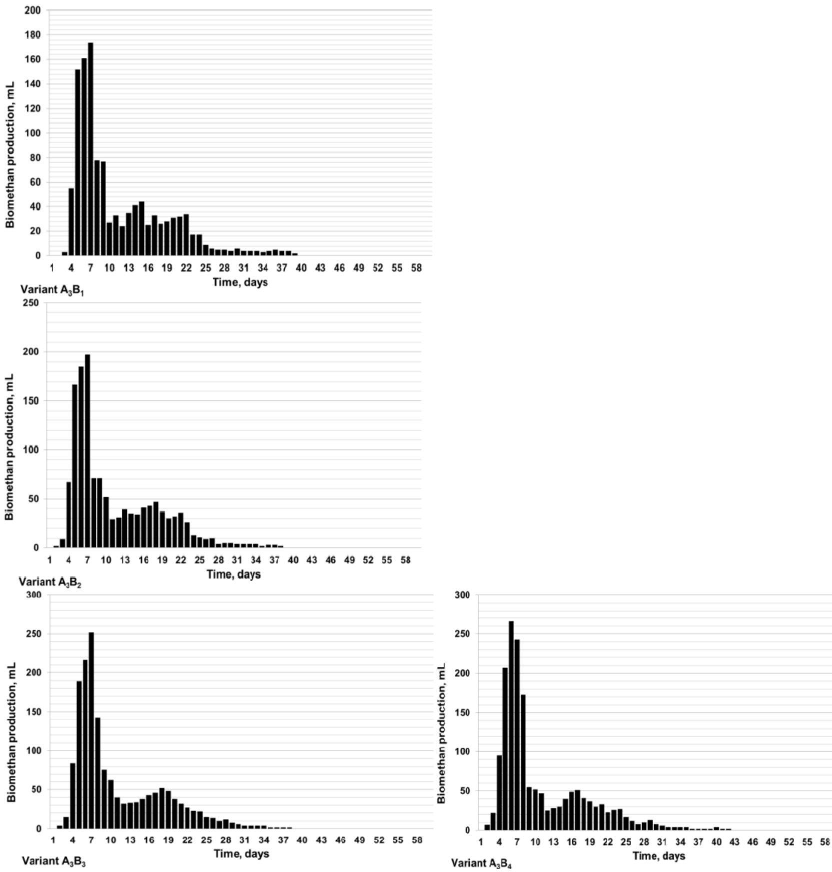



**Figure 5.21 – Biomethane production during the experimental period of oilseed rape silages (inoculum subtracted) obtained from plant mass of different sowing and harvesting dates (average adjusted for biomethane productivity of inoculum and standardized dry gas values for 2020–2022 for the total number of observations for each variant) (Tsytsiura, 2023a)**




**Continued Figure 5.21 – Biomethane production during the experimental period of oilseed rape silages (inoculum subtracted) obtained from plant mass of different sowing and harvesting dates (average adjusted for biomethane productivity of inoculum and standardized dry gas indicators for 2020–2022 for the total number of observations for each variant) (Tsytsiura, 2023a)**

Table 5.37

**Functional expression of the cumulative biomethane and biomethane productivity of oilseed radish silages (inoculum subtracted) obtained from plant mass of different sowing and harvesting periods (based on average data for the period 2020–2022) (Tsytsiura, 2023a)**

| Variant* | Equation of dependence on the time of anaerobic fermentation (t) | Parameters of the equation | | Statistical parameters for assessing the reliability of fitting the actual dynamics to the theoretical expression of the equation | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $y_m$ | $k_1$ | S | $R^2_{(adj.)}$ | RMSE | RRMSE | *p* |
| **cumulative biomethan production (y) at time t (mL)** | | | | | | | | |
| $A_1B_1$ | $y(t) = y_m\left(1 - e^{(-k_1 t)}\right)$ | 1625.533 | 0.122 | 45.700 | 0.985 | 128.91 | 18.96 | *<0.001* |
| $A_1B_2$ | | 1564.910 | 0.129 | 46.828 | 0.980 | 129.47 | 19.15 | *<0.001* |
| $A_1B_3$ | | 1473.787 | 0.129 | 62.617 | 0.961 | 132.28 | 19.58 | *<0.001* |
| $A_1B_4$ | | 1380.248 | 0.134 | 44.167 | 0.975 | 130.93 | 19.21 | *<0.001* |
| $A_2B_1$ | | 1917.568 | 0.097 | 54.127 | 0.982 | 129.11 | 19.07 | *<0.001* |
| $A_2B_2$ | | 1862.261 | 0.102 | 54.770 | 0.980 | 129.61 | 19.18 | *<0.001* |
| $A_2B_3$ | | 1784.985 | 0.111 | 78.609 | 0.961 | 132.37 | 19.64 | *<0.001* |
| $A_2B_4$ | | 1626.935 | 0.110 | 60.126 | 0.969 | 131.68 | 19.59 | *<0.001* |
| $A_3B_1$ | | 1265.749 | 0.080 | 73.296 | 0.950 | 134.94 | 19.97 | *<0.001* |
| $A_3B_2$ | | 1422.200 | 0.080 | 81.548 | 0.951 | 134.21 | 19.88 | *<0.001* |
| $A_3B_3$ | | 1635.270 | 0.068 | 96.530 | 0.950 | 135.11 | 20.05 | *<0.001* |
| $A_3B_4$ | | 1767.454 | 0.087 | 101.153 | 0.955 | 133.89 | 19.57 | *<0.001* |

**biomethan production (y) at time t (mL)**

| Variant* | Equation of dependence on the time of anaerobic fermentation (t) | Parameters of the equation | | | | Statistical parameters for assessing the reliability of the fitting | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | a | b | c | d | S | $R^2_{(adj.)}$ | RMSE | RRMSE | p |
| $A_1B_1$ | $y(t) = \frac{a + bt}{1 + ct + dt^2}$ | -5.721 | 5.070 | -0.322 | 0.028 | 12.476 | 0.952 | 78.96 | 8.69 | <0.001 |
| $A_1B_2$ | | -4.237 | 6.525 | -0.417 | 0.049 | 13.569 | 0.943 | 79.39 | 8.87 | <0.001 |
| $A_1B_3$ | | -2.131 | 7.891 | -0.496 | 0.068 | 13.968 | 0.936 | 81.12 | 9.14 | <0.001 |
| $A_1B_4$ | | -1.148 | 9.446 | -0.539 | 0.080 | 14.107 | 0.927 | 83.56 | 9.75 | <0.001 |
| $A_2B_1$ | | -40.878 | 41.926 | -0.547 | -0.108 | 9.951 | 0.961 | 76.97 | 8.35 | <0.001 |
| $A_2B_2$ | | -27.221 | 30.650 | -0.543 | 0.097 | 11.468 | 0.954 | 78.27 | 8.47 | <0.001 |
| $A_2B_3$ | | -2.497 | 8.973 | -0.433 | 0.052 | 12.319 | 0.960 | 77.18 | 8.59 | <0.001 |
| $A_2B_4$ | | -6.290 | 14.139 | -0.491 | 0.071 | 8.099 | 0.974 | 73.27 | 7.52 | <0.001 |
| $A_3B_1$ | | -3.877 | 3.804 | -0.275 | 0.019 | 14.563 | 0.905 | 90.49 | 11.18 | <0.001 |
| $A_3B_2$ | | -13.283 | 5.989 | -0.336 | 0.031 | 12.186 | 0.917 | 87.29 | 10.57 | <0.001 |
| $A_3B_3$ | | -4.278 | 4.741 | -0.309 | 0.024 | 13.741 | 0.914 | 88.14 | 10.91 | <0.001 |
| $A_3B_4$ | | -5.721 | 5.070 | -0.322 | 0.028 | 12.477 | 0.950 | 78.81 | 8.69 | <0.001 |

* – in accordance with the combinatorics of options according to Table 5.31

Conversely, for the green pod phase, with a decrease in crude protein content, an increase in crude fiber content, and a decrease in the content of nitrogen-free extractives, its value was in the range of 0.068–0.087. Due to this, the standard error of the graphs approximation naturally increases consistently when comparing the budding and flowering phenophases and confirms the conclusions drawn from the analysis of individual graphs of biomethane production for each experimental variant.

As for the mathematical analysis of the dynamics of biomethane production, taking into account the steady downward oscillatory dynamics, the presence of several peaks on the general downward curve, and the graphical dependence which was selected on the basis of the approximation process using the CurveExpert Professional software package is a linear and quadratic relationship that forms a complex curve configuration with a consistent peak increase at the 3–7$^{th}$ fixation point and a consistent steady decrease of hyperbolic character ($1(x(t)^{-1})$ (according to Gavril and Schönheim (1982)). This character of the curves, the level of approximation of which for all variants of the experiment was confirmed for the level of significance of 0.1% ($p<0.001$) indicates that the process of biomethane production from oilseed radish silage is an intensively decaying process, the main productive component of which is concentrated in the fixation cycle of 4–7 days, and the final process of productive biomethane production does not reach the full cycle of the selected experimental duration of anaerobic digestion (in our case, 60 days) (as indicated by the ratio of the coefficients a and b against the background of low values of the coefficients d according to Bardsley & Childs (1975)).

Additional indicators of the kinetics of biomethane production from oilseed radish silage (inoculum subtracted) (Table 5.38) allowed us to determine the features characteristic of oilseed radish in comparison with other traditional bioenergy crops from the cruciferous family. Thus, the previously analyzed indicator of methane concentration in the total biogas volume produced averaged 54.91% (with a range of 49.92–59.11%), which corresponds to the range of 53.9–57.3 for fodder radish determined by Herrmann et al. (2016) and determined by (Carvalho et al, 2011; Belle et al., 2015) at the level of 50–60 % for oilseed radish in single-component or multicomponent anaerobic digestion.

Taking into account that the controlled anaerobic process leads primarily to a gas mixture of 51–75% methane (Badger et al., 1979; Zubr, 1986; Mohanty et al., 2022) and for traditional cruciferous crops this figure ranges from 51.3-62.8% (Herrmann et al, 2016; Rahman et al., 2018; Kılıç et al., 2021; Ţîţei, 2021, 2022) oilseed radish biomass in the variant of preliminary sludge fermentation can be effectively utilized as a component of biogas production.

It has been established that from the point of view of the performance indicators of the kinetics of biogas production and the actual proportion of methane, it is optimal to harvest oilseed radish biomass with subsequent silage for biogas fermentation in the flowering phase (BBSN 64–67). For this phase, the average methane content in the total biogas production was 56.35%, with biochemical methane potential ($BMP_{Gomp}$) at 307.09 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$, specific methane yields (SMY) (Figure 5.31d) of 292.45 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ (share of SMY/$BMP_{Gomp}$ 95.23%) and maximum specific methane production rate ($R_m$) at 31.67 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$. The values of these indicators for the budding phase (BBCH 64–67) were 52.31%, 278.92 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$, 285.51 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ (the share of SMY/$BMP_{Gomp}$ 97.69%) and 25.72 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$, respectively. For the phenological phase of the green pod (BBCH 73–75) was at the level of 55.97%, 237.54 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$, 244.30 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ (share of SMY/ $BMP_{Gomp}$ 97.24%) and 25.80 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$, respectively.

The efficiency of biogas productivity varied within the sowing dates. Averaged over the phenological phases budding-green pod (BBCH 50–75) for the first sowing period, the parameters of biogas production performance were as follows: methane content 54.90% with biochemical methane potential ($BMP_{Gomp}$) at the level of 284.36 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$, specific methane yields (SMY) (Figure 3d) 272.53 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ (the share of SMY/ $BMP_{Gomp}$ 95.83%) and the maximum specific methane production rate ($R_m$) at the level of 27.64 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$. The ratio index for SMY and Rm in comparison to the first sowing term for the second to fourth sowing term, depending on the phenological phase of biomass selection, was at the level of 0.81–1.41 and 0.84–1.38, respectively. At the same time, taking into account the level of SMY (> 200 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$) according to the assessment of the potential of bioenergy crops (Amon et al., 2007; Vindis et al., 2009; Herrmann et al., 2016; Kılıç et al. 2021), all sowing dates of oilseed radish have a fairly high level of productive potential for biogas processing. According to the assessment of the maximum achievable potential for the phenological phase of budding and flowering, the first and second sowing dates had the optimum, and the third and fourth – for the green pod phase. This distribution pattern is primarily confirmed by the peculiarities of the biochemical composition of both raw biomass and biomass after silage fermentation. In particular, during the green pod phase, an intensive increase in the proportion of crude fiber was observed with a corresponding decrease in nitrogen-free extractives (NfE) (Tables 5.35–5.37).

Table 5.38

**Biomethane production characteristics of oilseed rape silages (inoculum subtracted) depending on the sowing date and phenological phase of plants (average for 2020–2022 for the total number of observations for each variant) (Tsytsiura, 2023a)**

| Sowing date | Methane content (%) | | $BMP_{Gomp}$ ($L_N$ $kg^{-1}_{ODM}$) | | $R_m$ ($L_N$ $kg^{-1}_{ODM}$ $d^{-1}$) | | $t_{50}$ (d)* | | Lag period (λ) (d)*** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\bar{x}$ | SD** | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD | $\bar{x}$ | SD |
| **budding stage (BBCH 50–53)** | | | | | | | | | | |
| I | 53.95 | 3.54 | 304.94 | 11.55 | 27.88 | 1.17 | 3.57 | 0.32 | 1.08 | 0.17 |
| II | $53.42^{d}$ | 4.53 | $298.97^{c}$ | 13.87 | $26.63^{b}$ | 1.29 | $2.96^{b}$ | 0.40 | $1.25^{c}$ | 0.13 |
| III | $51.96^{b}$ | 2.53 | $274.74^{b}$ | 14.17 | $24.98^{b}$ | 1.58 | $3.89^{c}$ | 0.25 | $1.51^{b}$ | 0.11 |
| IV | $49.92^{b}$ | 5.49 | $263.39^{b}$ | 14.35 | $23.40^{a}$ | 1.67 | $3.00^{c}$ | 0.25 | $1.47^{b}$ | 0.19 |
| flowering stage (BBCH 64–67) | | | | | | | | | | |
| I | 53.90 | 1.32 | 344.13 | 7.06 | 33.74 | 1.25 | 4.50 | 0.50 | 1.18 | 0.12 |
| II | $54.69^{c}$ | 1.98 | $314.19^{b}$ | 8.38 | $32.69^{b}$ | 1.39 | $4.35^{b}$ | 0.42 | $1.46^{c}$ | 0.15 |
| III | $59.11^{a}$ | 2.50 | $280.30^{a}$ | 9.68 | $31.58^{a}$ | 1.47 | $3.61^{a}$ | 0.38 | $1.75^{a}$ | 0.10 |
| IV | $57.69^{a}$ | 4.11 | $289.75^{a}$ | 11.90 | $28.67^{a}$ | 1.61 | $3.91^{a}$ | 0.44 | $1.58^{b}$ | 0.14 |
| green pod stage (BBCH 73–75) | | | | | | | | | | |
| I | 56.86 | 4.60 | 204.01 | 9.85 | 21.30 | 1.12 | 4.85 | 0.48 | 2.88 | 0.21 |
| II | $56.33^{c}$ | 2.72 | $222.29^{b}$ | 10.84 | $23.89^{b}$ | 1.21 | $5.38^{b}$ | 0.52 | $1.92^{b}$ | 0.17 |
| III | $55.27^{b}$ | 2.34 | $263.62^{a}$ | 13.84 | $28.55^{a}$ | 1.55 | $4.37^{c}$ | 0.63 | $1.83^{b}$ | 0.15 |
| IV | $55.42^{b}$ | 3.72 | $287.26^{a}$ | 14.98 | $29.46^{a}$ | 1.49 | $4.45^{c}$ | 0.58 | $1.71^{b}$ | 0.12 |

$BMP_{Gomp}$: biochemical methane potential derived from the modified Gompertz equation; Rm: maximum specific methane production rate; $^{*}t_{50}$: half-life (counting from the beginning of methane emission); **SD: standard deviation; ***: in terms of days from hourly accounting in the ratio of 1 day = 24 hours; Significance levels in comparison with the first (I) sowing term: a – 0.1%; b – 1%; c – 5%; d – no significant difference.

Another possible factor in the advantage of later sowing dates for harvesting at the green pod stage is the appearance of pods with seed germs in the structure of the leaf-stem mass. It is during the fruiting period that intensive synthesis of fatty acids begins in oilseed radish (Tsytsiura, 2022) and an intensive increase in the concentration of glycosaminolates from 50 to 160 μmol $g^{-1}$ is noted (Carlson et al., 1985; Prieto et al., 2019). Given the possible influence (inhibition) of glucosinolates on the intensity of biofermentation of the crude mass of cruciferous plant species (Barba et al. (2016); Sun et al. (2020); Bichsaem et al. (2021)). This issue may also be an additional factor in the reduction of SMY for oilseed radish at the fruiting stages (BBCH>70) and requires further study as it is an important factor in the effective use of traditional and less common cruciferous plant species for biofermentation for bioenergy needs.

Certain peculiarities were also noted for the indicator of anaerobic fermentation half-life ($t_{50}$). A number of studies have found that its value varies for different bioenergy crops in the range of 1.5–9.5 (Petersson et al., 2007; Vindis et al., 2009), and for cruciferous plants it ranges from 2.62–5.11, and in particular for fodder radish 2.68–3.69 (Carvalho et al., 2011; Herrmann et al., 2016). For oilseed radish, within the experimental variants, this indicator differed significantly (2.96–5.38) both in terms of biomass harvesting and sowing dates with a pronounced tendency of its growth (on average, in comparison with the budding phase (BBCH 50–53), the growth index was 1.22, and by the green pod phase (BBCH 73–75) it was 1.42) during the maturation of oilseed radish plants. Within the sowing dates, the trend is the opposite (the index of decrease in comparison with the first sowing date for the second term was 0.98, for the third term 0.92, for the fourth term 0.88). Based on this, a conclusion was made that confirms the analysis of the analysis of biomethane production graphs in terms of variants (Figure 5.21b) regarding the peak period in the anaerobic fermentation of oilseed radish silage on the 3rd–7th day of fixation, as well as the belonging of the kinetics of biomethane production from oilseed radish biomass to a high-amplitude pronounced damping process, which is consistent with the findings of Petersson et al. (2007) and Yen et al. This specificity of the process kinetics is also confirmed by the lag period (λ) in the range of 1.08–2.88 for different oilseed radish variants.

Such a short lag period was obtained in the study of Carvalho et al. (2011), where the process of biogas formation was observed on the second day after the laying of silage from oilseed radish biomass for anaerobic fermentation. This nature of the formation of the lag phase duration is explained by the results of Kim & Kim (2020), who found that the lag phase could be caused by the acidification by volatile fatty acid (VFA) accumulation and the initial VFA to volatile solid ratio. To reduce the lag-phase, the VFA/Alk ratio should be maintained below 0.4.

The initial VFA/VS ratio below 10% enhanced anaerobic digestion performance and digestion time reduction at a high protein loading rate. Taking into account the previous conclusions about the increase in both crude fat content and total fatty acid content due to the strengthening of fruit and seed formation subphases with a rich amino acid composition (Bell et al., 2000; Barthet & Daun, 2002; Ávila & Sodré, 2012) against the background of an increase in dry matter content during the green pod phase (BBCH 73–75), a longer lag period of 2.09 days (for comparison, the same indicator averaged by sowing dates for the flowering phase (BBCH 64–67) was 1.49 and for the budding phase (BBCH 73–75) – 1.33). The variable dynamics of the lag phase duration (λ) within the sowing dates is explained by the same reasons (according to Kim and Kim (2020)) for the ratio of biochemical components of silage-fermented oilseed radish leaf-stem mass noted in the assessment of the effect of sowing dates on the chemical composition of the silage substrate.

Based on the preliminary analysis, it should be noted that the biochemical composition of the substrate undergoing anaerobic fermentation will affect both the chemistry and the kinetics of the biogas formation process under appropriate temperature conditions. Such conclusions are consistent with the basic publications on this issue (Weißbach et al., 1995; Ofori and Becker, 2008; Carvalho et al. (2011); Rath et al, 2013; Dandikas et al. 2014; Herrmann et al. 2016; Lamba et al., 2016; Jankowska et al. 2017; Martínez-Gutiérrez 2018; Kılıç et al. 2021; Czubaszek et al. 2022; Lallement et al. 2023). The results of research in this area in the application to the anaerobic fermentation of oilseed radish silage are to some extent similar to the results of these scientists (Table 5.39). However, it should be noted that there are certain features that distinguish this system of indicators from the point of view of assessing the impact on the kinetics of the biomethane production process. Taking into account the values of the determined correlation coefficients, the SMY (specific methane yield) for oilseed radish silages (inoculum subtracted) was tendentially higher (the level of 'Moderate correlation' was taken into account (according to the recommendations of Dandikas et al, 2014)) with lower crude fiber content (CFb, coefficient of determination (dyx) 53.29%), higher organic dry matter (ODM, $d_{yx}$ 19.36%), organic acid derivatives (SBVa, $d_{yx}$ 20.25%; SAPa, $d_{yx}$ 30.25%), alcohols (Alc, $d_{yx}$ 23.04%), lactic acid (LA, $d_{yx}$ 18.49%), but despite the higher concentration of these acids at a lower acidity of the substrate (at a higher numerical pH value) (pH A, $d_{yx}$ 10.89%).

The $R_m$ (maximum methane production rate) was significantly higher with lower crude fiber content (CFb, coefficient of determination ($d_{yx}$) 40.96%), higher crude ash content (CA, $d_{yx}$ 18.49%), higher $k_1$ (first order decay constant, $d_{yx}$ 54.76%) and lower silage substrate acidity (pH A, $d_{yx}$ 7.80%). The $t_{50}$ (half-life period) was tendentially higher due to higher crude fiber content (CFb, $d_{yx}$ 53.29%), higher dry and organic dry matter content (DM, $d_{yx}$ 43.56%; ODM, $d_{yx}$ 29.16%), higher C/N ratio ($d_{yx}$ 57.76%), lower content of a number of organic acid derivatives and silage fermentation alcohols (SBVa, La, SAPa, Alc: $d_{yx}$ 28.09–67.24%), lower crude protein content (CP, $d_{yx}$ 49.00%), lower crude ash content (CA, $d_{yx}$ 60.84%), higher pH (lower acidity of the silage substrate) ($d_{yx}$ 62.41%) with a lower value of $k_1$ (first order decay constant, $d_{yx}$ 77.44%). The duration of the lag phase ($\lambda$) had the same dependence as the $t_{50}$ (half-life period) due to the identity of its formation mechanism in the anaerobic fermentation system (Kim & Kim (2020)).

According to the level of the direct (G) and adjusted (G′) correlation graph, it was determined that the productive indicators of biogas yield SMY and $R_m$ in the case of anaerobic fermentation of oilseed radish silage in the system of dependencies belong to the average deterministic ones in the applied complex of the correlation galaxy for 19 traits (according to Sokal & Rohlf, 2012; Lockwood, 2016)) with the level of determination according to the adjusted correlation graph (G′) at the level of 19.62% and 23.62%.

Table 5.39

**Pearson's correlation coefficients of chemical components and methane production characteristics of all crop silage samples (for a joint system of matching variants–repetitions–years (N=144)) (Tsytsiura, 2023a)**

| 1. DM* | 2. ODM | 3. CP | 4. CF | 5. CFb | 6. CA | 7. NfE | 8. C/N | 9. SBVa | 10. Alc | 11. pH | 12. La | 13. SAPa | 14. $y_m$ | 15. $k_1$ | 16. MC | 17. SMY | 18. $R_m$ | 19. $t_{50}$ | 20. λ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 200 |
| 1 | 0.59 | -0.69 | 0.36 | 0.66 | -0.60 | 0.12 | 0.54 | -0.79 | -0.77 | 0.78 | -0.79 | -0.70 | 0.08 | -0.52 | 0.50 | -0.43 | 0.04 | 0.66 | 0.60 |
| 2 | | -0.68 | 0.33 | 0.69 | -0.61 | 0.63 | 0.73 | -0.77 | -0.74 | 0.75 | -0.78 | -0.68 | 0.26 | -0.61 | 0.69 | 0.44 | 0.22 | 0.54 | 0.52 |
| 3 | | | -0.26 | -0.71 | 0.93 | -0.66 | -0.99 | 0.62 | 0.56 | -0.59 | 0.64 | 0.41 | 0.44 | 0.80 | -0.34 | 0.24 | 0.17 | -0.70 | -0.41 |
| 4 | | | | 0.24 | -0.30 | 0.08 | 0.31 | -0.36 | -0.26 | 0.39 | -0.38 | -0.28 | -0.18 | -0.26 | 0.28 | -0.37 | -0.16 | 0.48 | 0.34 |
| 5 | | | | | -0.80 | 0.12 | 0.77 | -0.80 | -0.79 | 0.78 | -0.83 | -0.73 | -0.38 | -0.84 | 0.59 | -0.73 | -0.64 | 0.73 | 0.77 |
| 6 | | | | | | -0.61 | -0.92 | 0.74 | 0.67 | -0.72 | 0.76 | 0.52 | -0.01 | 0.86 | -0.40 | 0.22 | 0.43 | -0.78 | -0.48 |
| 7 | | | | | | | 0.59 | -0.06 | 0.04 | 0.08 | -0.08 | 0.27 | 0.02 | -0.32 | -0.03 | 0.36 | 0.01 | 0.29 | -0.29 |
| 8 | | | | | | | | -0.66 | -0.60 | 0.64 | -0.69 | -0.48 | -0.32 | -0.84 | 0.41 | -0.24 | -0.32 | 0.76 | 0.45 |
| 9 | | | | | | | | | 0.79 | -0.78 | 0.75 | 0.72 | -0.06 | 0.86 | -0.66 | 0.45 | -0.02 | -0.82 | -0.80 |
| 10 | | | | | | | | | | -0.76 | 0.77 | 0.73 | -0.06 | 0.84 | -0.63 | 0.48 | -0.01 | -0.76 | -0.81 |
| 11 | | | | | | | | | | | -0.69 | -0.61 | 0.16 | -0.67 | 0.75 | 0.33 | 0.28 | 0.79 | 0.77 |
| 12 | | | | | | | | | | | | 0.52 | -0.18 | 0.69 | -0.63 | 0.43 | -0.05 | -0.53 | -0.50 |
| 13 | | | | | | | | | | | | | -0.07 | 0.76 | -0.64 | 0.55 | -0.02 | -0.66 | -0.56 |
| 14 | | | | | | | | | | | | | | -0.18 | 0.60 | 0.75 | 0.82 | 0.08 | -0.34 |
| 15 | | | | | | | | | | | | | | | -0.58 | 0.25 | 0.74 | -0.88 | -0.62 |
| 16 | | | | | | | | | | | | | | | | -0.22 | 0.20 | 0.45 | 0.66 |

(End of Table 5.39)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 200 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 17 | | | | | | | | | | | | | | | | | 0.78 | -0.37 | -0.82 |
| 18 | | | | | | | | | | | | | | | | | | -0.52 | -0.56 |
| 19 | | | | | | | | | | | | | | | | | | | 0.57 |
| **10.2 | 11.2 | 10.8 | 5.6 | 12.6 | 11.4 | 4.7 | 11.3 | 11.5 | 11.1 | 11.1 | 10.7 | 9.9 | 5.0 | 12.1 | 9.3 | 8.4 | 5.8 | 11.4 | 11.0 |
| ***0.64 | 0.59 | 0.57 | 0.31 | 0.70 | 0.63 | 0.58 | 0.59 | 0.72 | 0.69 | 0.65 | 0.63 | 0.58 | 0.42 | 0.64 | 0.51 | 0.44 | 0.49 | 0.63 | 0.57 |

r = |0|–|0.4| No or weak correlation; r = |0.4|–|0.7| Moderate correlation; r = |0.7|–|1.0| Strong correlation. *DM: dry matter; ODM: organic dry matter; CF: crude fat; CP: crude protein; CFb: crude fibre; CA: crude ash; NfE: nitrogen-free extracts; C/N: carbon to nitrogen ratio; SBVa: sum of i-butyric, butyric, i-valeric, valeric and caproic acid; Alc: Sum of ethanol, propanol, 1,2-butanediol, 2,3-propanediol; pH: silage acidity; LA: lactic acid; SAPa: sum of acetic and propionic acid; $y_m$: is the maximum specific methane yield at theoretically infinite digestion time; $k_1$: first order decay constant; MC: methane content; SMY: specific methane yield; $R_m$: maximum methane production rate; $t_{50}$: half-life period; λ: lag phase period. ** Graf G; *** Graf G´. For a significance level of $p < 0.05$, the interval r = 0.16–0.20, for $p < 0.01$ r = 0.21–0.26, for $p < 0.001$ r > 0.26.

At the same time, the highest levels of determination were established for such indicators as $k_1$ t50 and λ with the corresponding value of the general correlation graph (G) at the level of 11.0–12.1 with the level of determination by the adjusted correlation graph (G´) at the level of dyx 32.72–40.70%. In the system of factor indicators, the highest level of determination by the size of the correlation graphs was established for the crude fiber content (CFb) (G at the level of 12.6, and G´ in the expression dyx 49.00%).

It should be noted that the acidity (pH) of the oilseed radish silage samples has a tendency to influence the biomethane productivity of substrates. Based on the fact that silages from cruciferous crops have a predominantly pH in the range of 3.5–5.3 and for radish 3.8–5.3 (Herrmann et al, 2016), optimization of silage acidity to the level of 4.6–5.0 positively affects the levels of biomethane production in terms of SMY and $R_m$ and, given the established dependencies, allows for their conjugate growth with a decade-long decrease in acidity (respectively, an increase in the nominal pH) by at least 9.0–11.0%. These conclusions are consistent with the findings of Jayaraj et al. (2014), Cerón-Vivas et al. (2019), and Zhang et al. (2022).

The presence of a complex variation in the size of correlation graphs allowed us to conclude that the dependencies between the factors taken for the analysis of the kinetics and productivity of biomethane production from silage-fermented oilseed radish mass are more complex. Based on this, a system of graphical regression correlation of a number of indicators to the resulting SMY (specific methane yield, $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$) was applied using the method of weighted least squares distances (Figure 5). The presented regression surfaces demonstrated the complex nature of the formation of the main resulting indicator SMY (specific methane yield) from the binary combination of a number of biochemical parameters of oilseed radish silage in the systematic comparison of the general combinatorics of options. Thus, in the system of dependencies SMY–C/N–NfE (Figure 5.22a), the maximum level of SMY (330–350 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$) is predicted to be formed at the content of nitrogen-free extractives (NfE) in the silage mass of oilseed radish at the level of 50–52$\%_{DM}$ at a C/N ratio of 20–22.

For the system of SMY–NfE–CP dependencies (Figure 5.22b), the same level of SMY can be predictably achieved at the following NfE values of 50–52$\%_{DM}$ at a crude protein content (CP) of 15–16$\%_{DM}$.

For the system of SMY–CF–NfE dependencies (Figure 5.22c), the level of SMY 312–340 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ can be predictably achieved at the following values of the comparison factors NfE 48–50$\%_{DM}$, crude fat (CF) 3.1–3.2$\%_{DM}$.

For the SMY–CFb–NfE dependence system (Figure 5.22d), the level of SMY > 300 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$can be predictably achieved with the following values of the matching factors NfE 50–52$\%_{DM}$ and crude fiber (CFb) 20–23$\%_{DM}$.

For the system of SMY–CA–NfE dependencies (Figure 5.22e), the level of SMY >300 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ can be predictably achieved at the following values of the matching factors CA 14–16$\%_{DM}$ and NfE 48–50$\%_{DM}$.

For the SMY–CF–CP system (Figure 5.22f), the level of the maximum resulting SMY index >300 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ is achievable at CF values of 3.2–3.35$\%_{DM}$ and CP values of 14–16$\%_{DM}$.

For the SMY–CFb–CP system (Figure 5.22g), the maximum resulting SMY > 360 $L_N$ $kg^{-1}{}_{ODM}$ $d^{-1}$ is achieved at CFb 18–22$\%_{DM}$ and CP 8–12$\%_{DM}$.

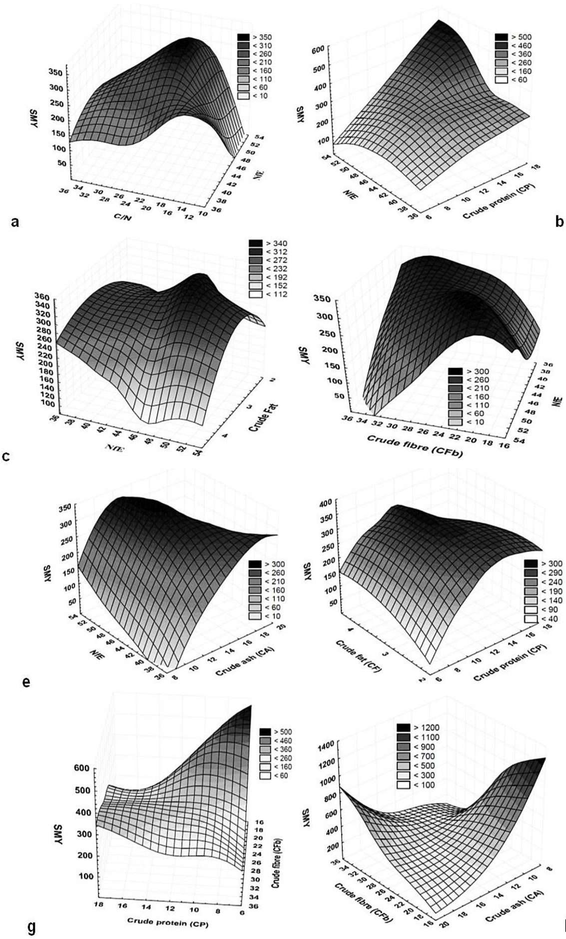



**Figure 5.22 – Response surfaces of dependencies (method of weighted least squares distances) of the ‘specific methane yield’ (SMY) indicator depending on the basic chemical composition of oilseed radish silages (inoculum subtracted) (in the summary system of variants–repeat–years). Regression comparisons: a: SMY–C/N–NfE; b: SMY– NfE–CP; c: SMY–CF–NfE; d: SMY–CFb–NfE; e: SMY–CA–NfE; f: SMY–CF–CP; g: SMY–CFb–CP; h: SMY–CFb–CA (Tsytsiura, 2023a)**

For the SMY–CFb–CA system (Figure 5.22h), the level of maximum resulting SMY up to 500 $L_N$ $kg^{-1}_{ODM}$ $d^{-1}$ is achieved at CFb 16–18%$_{DM}$ and crude ash (CA) 10–12%$_{DM}$ or (binary peak reaction surface) in the variant: CFb 26–28%$_{DM}$ and CA 18–20%$_{DM}$.

The constructed reaction surfaces are fully consistent with the results of the evaluation of a significant number of bioenergy crops for biogas productivity (Herrmann et al., 2016; Oleszek et al., 2020; Aravani et al., 2021; Lallement et al., 2023) and take into account the special characteristics of oilseed radish under different technological solutions, taking into account the timing of sowing and the timing of leaf mass selection for anaerobic fermentation.

Oilseed radish as a multidisciplinary bioenergy crop has demonstrated high biogas and biomethane potential with the possibility of long-term use and biomass harvesting in a wide range of phenological phases. From the point of view of the potential share of methane yield in combination with biogas productivity for the phenological phase of budding (BBCH 50–53) and flowering (BBCH 64–67) with the subsequent process of silage fermentation, the variant of the first sowing term with the level of biochemical methane potential ($BMP_{Gomp}$), respectively, 304.94 and 344.13 $L_N$ $kg^{-1}_{ODM}$ $d^{-1}$, specific methane yield (SMY) 296.91 and 319.66 $L_N$ $kg^{-1}_{ODM}$ $d^{-1}$ with a maximum specific methane production rate ($R_m$) 27.88 and 33.74 $L_N$ $kg^{-1}_{ODM}$ $d^{-1}$. For the phenological phase of the green pod (BBCH 73–75), the variant of the fourth sowing term (summer term as a possible option for intermediate cultivation of oilseed radish in crop rotation) with the corresponding parameters was determined as expedient: $BMP_{Gomp}$ 287.26 $L_N$ $kg^{-1}_{ODM}$ $d^{-1}$, SMY 283.18 $L_N$ $kg^{-1}_{ODM}$ $d^{-1}$ at $R_m$ 29.46 $L_N$ $kg^{-1}_{ODM}$ $d^{-1}$.

The optimal biochemical idiotype of oilseed radish plants was determined in the system of pairwise correlation and multiple regression comparison from the point of view of realization of biomethane potential of the crop when harvesting its biomass in the interphase period of budding–green pod (BBCH 50–75): CP 14–18%$_{DM}$, CFb 16–20%$_{DM}$, CA 14–18%$_{DM}$, CF 3.1–3.2%$_{DM}$, NfE 48–50%$_{DM}$ at a C/N ratio of 20–22 with the acidity of the subsequent silage-fermented mass at the level of pH 4.6–5.0.

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